# HERBICIDAL COMPOSITIONS CONTAINING GLYPHOSATE AND A PYRIDINE ANALOG

## REFERENCE TO RELATED APPLICATION

This application claims priority from U.S. Provisional Application Serial No. 60/496,031 (filed on April 22, 2003), and U.S. Provisional Patent Application Serial No. 60/552,065 (filed March 10, 2004), the entire contents of which are incorporated herein by reference.

## BACKGROUND OF THE INVENTION

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The present invention relates generally to herbicidal compositions or formulations, and to methods of using such compositions to kill, or control the growth and proliferation of, unwanted plants. In particular, the present invention relates to herbicidal compositions, as well as their methods of use, which comprise N-phosphonomethylglycine, or a herbicidal derivative thereof, and a pyridine analog, or a herbicidal derivative thereof, optionally with one or more suitable surfactants. Such compositions cause early visual symptoms of treatment and/or enhanced effectiveness or control when applied to the foliage of plants.

Herbicidal compositions comprising the herbicide N-phosphonomethyl-glycine or derivatives thereof ("glyphosate"), are useful for suppressing the growth of, or killing, unwanted plants such as grasses, weeds and the like. Glyphosate typically is applied to the foliage of the target plant. After application the glyphosate is absorbed by the foliar tissue of the plant and translocated throughout the plant. Glyphosate noncompetitively blocks an important biochemical pathway which is common to virtually all plants, but which is absent in animals. Although glyphosate is very effective in killing or controlling the growth of unwanted plants, the uptake (i.e., absorption) of glyphosate by the plant foliar tissue and translocation of glyphosate throughout the plant is relatively slow. Visual symptoms that a plant has been treated with glyphosate may not appear until one week or more after treatment.

Compositions comprising glyphosate may be formulated with one or more surfactants to enhance their effectiveness for foliar application. When water is added to a composition formulated with surfactants, the resulting sprayable composition more easily and effectively covers the foliage (e.g., the leaves or other photosynthesizing organs) of plants. Glyphosate salts, for example, have been formulated with surfactants such as polyoxyalkylene-type surfactants including, among other surfactants, polyoxyalkylene alkylamines. Commercial formulations of

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glyphosate herbicide marketed under the trademark ROUNDUP® have been formulated by Monsanto with such a polyoxyalkylene alkylamine, in particular a polyoxyethylene tallowamine.

As a result of the somewhat slow development of visual symptoms that may result when glyphosate is utilized alone, formulations or compositions containing glyphosate and another herbicide have been suggested, in an attempt to achieve both early visual symptoms of plant treatment and prolonged control of the plant. For example, some have suggested using a tank mix composition containing glyphosate and a contact herbicide, such as a pyridine analog like triclopyr (i.e., [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid) or a herbicidal derivative thereof. However, to-date, such tank mixes have generally (i) employed relatively low weight ratios of glyphosate to, for example, triclopyr (wherein glyphosate and triclopyr are present in equal amounts, glyphosate is in a slight excess, or triclopyr is in excess), and/or (ii) not utilized a surfactant therein.

For example, R.K. Howell et al. (Southern Weed Science Society Proceedings, 195-197 (1998)) disclose the preparation of a tank mixture containing a surfactant TL90, Roundup Pro® and Garlon™ 4, the glyphosate (in Roundup Pro®) and triclopyr (in Garlon™ 4) being present in an apparent weight ratio of approximately 1.3:1, respectively.

G.M. Wright et al. (North Central Weed Control Conference Proceedings, vol. 38, 139 (1983)) disclose the preparation of a tank mixture of glyphosate and triclopyr in the apparent absence of a surfactant, the glyphosate and triclopyr, respectively, being present in an apparent weight ratio of approximately 1.5:1.

M.L. McCormack et al. (Northeastern Weed Society Proceedings, vol. 36, 209-214 (1982)) disclose the preparation of a tank mixture of glyphosate and triclopyr in the apparent absence of a surfactant, the glyphosate and triclopyr, respectively, being present in an apparent weight ratio of approximately 1.4:1.

J. Lawrie et al. (Weed Research, vol. 33, 25-34, (1993) appear to disclose the preparation of a tank mixture of glyphosate, triclopyr and a surfactant-containing mixture, wherein the glyphosate and triclopyr, respectively, appear to be present in a weight ratio of approximately 1.67:1.

W. Harahap et al. (Biotrop Special Publication, no. 24, 317-24 (1986)) disclose the preparation of tank mixtures of glyphosate and triclopyr or picloram, in the apparent absence of a surfactant. In the tank mixtures, glyphosate and triclopyr are, respectively, present in an apparent weight ratio of approximately 9.5:1 or 11.5:1, while glyphosate and picloram are present in an apparent weight ratio of approximately 7.7:1.

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S.H. Kay et al. (Southern Weed Science Society Proceedings, 291 (1992)) disclose the preparation of a tank mixture of glyphosate and triclopyr in the apparent absence of a surfactant, the glyphosate and triclopyr, respectively, being present in a weight ratio of approximately 1:1.

A Roundup Pro® Supplemental Label (for application in California using a helicopter, EPA Reg. No. 524-475, Monsanto Company (1996)), discloses the optional preparation of a tank mixture of Roundup Pro® and Garlon™ 4 in varying weight ratios of glyphosate and triclopyr, respectively, as well as varying concentrations related thereto.

Tank mixtures require the user to purchase and store each herbicide used in the mixture separately, until the actual preparation of such mixtures in the field. The user must also measure out varying amounts of each herbicide used in the mixture. Therefore, a pre-packaged mixture (i.e., a concentrate) which already contains the desired herbicides in a single container may be desirable in some instances. However, concentrates may be difficult to prepare, for example when one of the herbicides is not soluble or miscible with the same desired solvent (e.g., water).

The solubility or miscibility problems sometimes encountered with concentrates may be overcome by preparing a concentrated emulsion formulation. A concentrated emulsion formulation consists of two phases and is a dispersion of one immiscible liquid (i.e., the discontinuous phase) in a second liquid (i.e., the continuous phase). If the continuous phase is water, the emulsion is an oil-in-water type emulsion and the water-immiscible liquid or solution may be referred to as the "oil" phase (regardless of its composition). In a concentrated emulsion formulation, the active ingredient may be dissolved in an organic solvent along with added emulsifiers and/or dispersants. When the concentrate is added to water, the active ingredient becomes dispersed throughout the water. Such a concentrate, in the form of a microemulsion, was prepared in U.K. Patent Application No. GB 2 267 825 A, using a slight excess of the isopropylamine salt of glyphosate relative to the butoxyethyl ester of triclopyr (weight ratio of glyphosate to triclopyr approximately 1.6:1), and a high load or amount of triclopyr and two ethoxylated cocoamine surfactants, Ethomeen™ C-15 and C-25 (approximately 100 g/L triclopyr and approximately 285 g/L total surfactant).

# SUMMARY OF THE INVENTION

Briefly, therefore, the present invention is directed to an aqueous herbicidal liquid concentrate, which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate comprises glyphosate, or a herbicidal derivative thereof, in a concentration of at

least about 50 grams acid equivalent per liter, a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof, and at least one surfactant, wherein (i) the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 1.7:1, and (ii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, an alkylamine salt, a  $C_{3-16}$  alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

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The present invention is further directed to an aqueous herbicidal liquid concentrate, which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate comprises glyphosate, or a herbicidal derivative thereof, in a concentration of at least about 50 grams acid equivalent per liter, a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof, and at least one surfactant, wherein (i) the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio ranging from at least 1.7:1 to less than about 32:1, and (ii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, a di-ammonium salt, an alkylamine salt, a  $C_{3-16}$  alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal liquid concentrate, which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate comprises glyphosate, or a herbicidal derivative thereof, a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof, and at least one surfactant in a concentration ranging from about 1 grams to 283 grams per liter, wherein (i) the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 1:1, glyphosate being in excess, and (ii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal liquid concentrate, which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate

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comprises glyphosate, or a herbicidal derivative thereof, a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof, in a concentration ranging from about 1 gram to 99 grams (acid equivalent basis) per liter, and at least one surfactant, wherein (i) the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 1:1, glyphosate being in excess, and (ii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, a di-ammonium salt, an alkylamine salt, a  $C_{3-16}$  alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal liquid concentrate, which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate comprises glyphosate, or a herbicidal derivative thereof, a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof, and at least one surfactant, wherein (i) the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 1:1, (ii) the glyphosate (acid equivalent basis) and the surfactant are present in a weight ratio of at least 1:1, wherein glyphosate is in excess in both instances, and (iii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a C<sub>3-16</sub> alkanolammonium salt, a diammonium salt, an alkylamine salt, a C<sub>3-16</sub> alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal liquid concentrate, which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate comprises glyphosate, or a herbicidal derivative thereof, and a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof, wherein the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 1:1, glyphosate being in excess, and further wherein (i) the pyridine analog or a herbicidal derivative thereof is present at a concentration of not greater than 99 grams (acid equivalent) per liter, and (ii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, an alkylamine salt, a  $C_{3-16}$  alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

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The present invention is still further directed to an aqueous herbicidal liquid concentrate, which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate comprises glyphosate, or a herbicidal derivative thereof, and a pyridine analog, or a herbicidal derivative thereof, wherein the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 1:1, glyphosate being in excess, and further wherein (i) the glyphosate (acid equivalent basis) or herbicidal derivative thereof is present at a concentration of not greater than 165 grams (acid equivalent) per liter, and (ii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a C<sub>3-16</sub> alkanolammonium salt, a di-ammonium salt, an alkylamine salt, a C<sub>3-16</sub> alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

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The present invention is still further directed to an aqueous herbicidal liquid concentrate which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate comprises at least one glyphosate salt predominantly in the form of potassium glyphosate, monoethanolamine glyphosate, or a mixture thereof; a pyridine analog selected from the group consisting of triclopyr, clopyralid, fluroxypyr, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof; and, at least one surfactant in a concentration less than 20 grams per liter; wherein the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 1:1, glyphosate being in excess.

The present invention is futher directed to an aqueous herbicidal liquid concentrate, which may be diluted with water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The concentrate comprises glyphosate, or a herbicidal derivative thereof, in a concentration of less than 65 grams acid equivalent per liter, picloram, or a herbicidal derivative thereof, and at least one surfactant, wherein (i) the glyphosate (acid equivalent basis) and the picloram (acid equivalent basis) are present in a weight ratio of at least 1:1, with glyphosate being in excess. Optionally, when the glyphosate is predominantly in the form of a salt, said salt may be selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, an alkylamine salt, a C<sub>3-16</sub> alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to a method of killing or controlling weeds or unwanted vegetation. The method comprises diluting one of the preceding liquid concentrates in a convenient amount of water to form an

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application mixture, and then applying a herbicidally effective amount of the application mixture to the foliage of the weeds or unwanted vegetation.

The present invention is still further directed to an aqueous herbicidal composition useful for killing or controlling the growth of unwanted plants. The composition comprises glyphosate, or a herbicidal derivative thereof, a pyridine analog, or a herbicidal derivative thereof, and at least one surfactant, wherein (i) the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 7.6:1, and (ii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a C<sub>3-16</sub> alkanolammonium salt, a di-ammonium salt, an alkylamine salt, a C<sub>3-16</sub> alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal composition useful for killing or controlling the growth of unwanted plants. The composition comprises glyphosate, or a herbicidal derivative thereof, a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof, in a concentration of not greater than 3.9 grams (acid equivalent basis) per liter, and at least one surfactant, wherein (i) the glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least about 1:1, glyphosate being in excess, and (ii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, a di-ammonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal composition useful for killing or controlling the growth of unwanted plants. The composition comprises glyphosate, or a herbicidal derivative thereof, a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof, and at least one surfactant, wherein (i) the surfactant concentration is not greater than 3.9 grams per liter, (ii) glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 3:1, and (iii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, a diammonium salt, an alkylamine salt, a  $C_{3-16}$  alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

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The present invention is still further directed to an aqueous herbicidal composition useful for killing or controlling the growth of unwanted plants. The composition comprises glyphosate, or a herbicidal derivative thereof, a pyridine analog, or a herbicidal derivative thereof, and at least one surfactant, wherein (i) the surfactant concentration is not greater than 6.6 grams per liter, (ii) glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 5:1, and (iii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, an alkylamine salt, a  $C_{3-16}$  alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal composition useful for killing or controlling the growth of unwanted plants. The composition comprises glyphosate, or a herbicidal derivative thereof, a pyridine analog, or a herbicidal derivative thereof, and at least one surfactant, wherein (i) the surfactant concentration is not greater than 9.3 grams per liter, (ii) glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 7:1, and (iii) when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a  $C_{3-16}$  alkanolammonium salt, an alkylamine salt, a  $C_{3-16}$  alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal composition useful for killing or controlling the growth of unwanted plants. The composition comprises glyphosate or a herbicidal derivative thereof, a pyridine analog or a herbicidal derivative thereof, and at least one surfactant, wherein either (i) the glyphosate concentration (acid equivalent basis) is not greater than 16.2 grams per liter, and glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 4:1, or (ii) the glyphosate concentration (acid equivalent basis) is not greater than 23.8 grams per liter, and glyphosate (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 6:1, and further when the glyphosate is predominantly in the form of a salt, said salt is selected from the group consisting of a sodium salt, an ammonium salt, an alkylammonium salt, a C<sub>3-16</sub> alkanolammonium salt, a di-ammonium salt, an alkylamine salt, a C<sub>3-16</sub> alkanolamine salt, an alkylsulfonium salt, a sulfoxonium salt, and combinations thereof.

The present invention is still further directed to an aqueous herbicidal composition useful for killing or controlling the growth of unwanted plants. The

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concentrate comprises at least one glyphosate salt predominantly in the form of potassium glyphosate, monoethanolamine glyphosate, or a mixture thereof; and a pyridine analog selected from the group consisting of triclopyr, clopyralid, fluroxypyr, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof; wherein (i) the glyphosate salt is present in a concentration less than 180 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 1:1, glyphosate being in excess; (ii) the glyphosate salt is present in a concentration less than 240 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 2:1; (iii) the glyphosate salt is present in a concentration less than 270 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 3:1; (iv) the glyphosate salt is present in a concentration less than 288 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 4:1; (v) the glyphosate salt is present in a concentration less than 300 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 5:1; (vi) the glyphosate salt is present in a concentration less than 308 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 6:1; (vii) the glyphosate salt is present in a concentration less than 315 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 7:1; (viii) the glyphosate salt is present in a concentration less than 320 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 8:1; (ix) the glyphosate salt is present in a concentration less than 324 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 9:1; or (x) the glyphosate salt is present in a concentration less than 326 grams acid equivalent per liter and the glyphosate salt (acid equivalent basis) and the pyridine analog (acid equivalent basis) are present in a weight ratio of at least 10:1.

The present invention is still further directed to a method for killing or controlling the growth of unwanted plants. The method comprises contacting the foliage of said plants with a herbicidally effective amount of one of the previously described aqueous herbicidal compositions.

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The present invention is still further directed to a herbicidal particulate solid concentrate which may be dissolved or dispersed in water to provide an aqueous herbicidal application mixture for application to the foliage of a plant. The solid concentrate comprises glyphosate, or a herbicidal derivative thereof, and a pyridine analog, or a herbicidal derivative thereof, wherein a weight ratio (a.e. basis) of glyphosate to the pyridine analog is at least about 1:1, glyphosate being in excess, and further wherein when the glyphosate is predominantly in the form of a salt. Optionally, one or more surfactants may be present in the herbicidal particulate solid concentrate.

The present invention is still further directed to a method of killing or controlling weeds or unwanted vegetation. The method comprises diluting or dissolving the previously described solid particulate concentrate in a convenient amount of water to form an application mixture, and then applying a herbicidally effective amount of the application mixture to the foliage of the weeds or unwanted vegetation.

The present invention is still further directed to one or more of the previously noted methods for killing or controlling the growth of unwanted plants which comprises contacting the foliage of said plants with such an aqueous herbicidal composition, wherein said herbicidal composition is brought into contact with, or applied to, said foliage using means other than a helicopter.

The present invention is still further directed to a method of killing or controlling weeds or unwanted plants. The method comprises diluting an aqueous herbicidal concentrate composition in an amount of water to form an application mixture; and, applying a herbicidally effective amount of the application mixture to foliage of the weeds or unwanted plants, wherein the weeds or unwanted plants comprise poison ivy, poison oak, kudzu, multiflora rose, golden rod, blue fescue, red maple, and/or red oak, and the aqueous herbicidal concentrate composition comprises glyphosate or a herbicidal derivative thereof; a pyridine analog selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr and picloram, or a herbicidal derivative thereof; and, at least one surfactant.

The present invention is still further directed to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein said pyridine analog is triclopyr, a derivative thereof, or some combination which includes triclopyr.

The present invention is still further directed to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein

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said pyridine analog is clopyralid, a derivative thereof, or some combination which includes clopyralid.

The present invention is still further directed to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein said pyridine analog is dithiopyr, a derivative thereof, or some combination which includes dithiopyr.

The present invention is still further directed to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein said pyridine analog is thiazopyr, a derivative thereof, or some combination which includes thiazopyr.

The present invention is still further directed, where appropriate, to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein said pyridine analog is picloram, a derivative thereof, or some combination which includes picloram.

The present invention is still further directed, where appropriate, to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein said pyridine analog is fluroxypyr, a derivative thereof, or some combination which includes fluroxypyr.

The present invention is still further directed, where appropriate, to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein said pyridine analog is a combination or mixture of one or more of triclopyr, fluroxypyr, dithiopyr, thiazopyr, picloram, or derivatives thereof.

The present invention is still further directed, where appropriate, to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein said pyridine analog is a combination or mixture of triclopyr and clopyralid, or derivatives thereof.

The present invention is still further directed, where appropriate, to one or more of the previously described aqueous herbicidal liquid concentrates, aqueous herbicidal compositions, herbicidal particulate solid concentrates, and methods for the use thereof, wherein said pyridine analog is a combination or mixture of one or more of triclopyr, clopyralid, fluroxypyr, or derivatives thereof.

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#### DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, coherbicidal compositions or formulations containing glyphosate or a derivative thereof, a pyridine analog (e.g., triclopyr, clopyralid, fluroxypyr, dithiopyr, thiazopyr, picloram, etc., or a combination thereof) or a derivative thereof, and optionally a suitable surfactant, are provided that are advantageous for a number of reasons, including rapid uptake by the target plant, early visual symptoms of plant treatment, and control of a broad spectrum of plant species, as well as enhanced, more consistent control of unwanted plants.

Accordingly, in at least some embodiments, lower application rates may potentially be used for the pyridine analog and/or the surfactant(s) applied, without a loss of effectiveness of plant control.

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## Glyphosate and Pyridine Analog Coherbicides

## A. Coherbicide Combinations and Forms

The compositions or formulations of the present invention comprise at least two herbicides, and optionally at least one surfactant. A first component of the compositions of the present invention may be, for example,

N-phosphonomethylglycine ("glyphosate"), a salt or adduct thereof, or a compound which is converted to glyphosate in plant tissues or which otherwise provides glyphosate ion. In this regard it is to be noted that the term "glyphosate," when used herein, is to be understood to encompass such derivatives unless the context requires otherwise.

Glyphosate salts that can be used according to this invention include but are not restricted to, for example, alkali metal salts, for example sodium and potassium salts, ammonium salts, alkylammonium salts (e.g.,  $C_{1-16}$  alkylammonium, or alternatively  $C_{3-16}$  alkylammonium), alkanolammonium salts (e.g.,  $C_{1-16}$  alkanolammonium, or alternatively  $C_{3-16}$  alkanolammonium), di-ammonium salts such as dimethylammonium, alkylamine salts, for example dimethylamine and isopropylamine salts, alkanolamine salts (e.g.,  $C_{1-16}$  alkanolamine, or alternatively  $C_{3-16}$  alkanolamine), for example ethanolamine salts, alkylsulfonium salts (e.g.,  $C_{1-16}$  alkylsulfonium, for example trimethylsulfonium salts), sulfoxonium salts, and mixtures or combinations thereof. For some preferred embodiments, preferred glyphosate salts include for example the potassium salt, isopropylamine salt, ammonium salt, di-ammonium salt, sodium salt, monoethanolamine salt, and trimethylsulfonium salt, as well as combinations thereof. For still other preferred embodiments, glyphosate is predominantly in the form of a salt other than a

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potassium salt or a monoethanolamine or monoethanolammonium salt; that is, in an alternative preferred embodiment glyphosate is a salt predominantly in the form of the isopropylamine salt, the ammonium salt, the di-ammonium salt, the sodium salt, the trimethylsulfonium salt, or some combination thereof.

The herbicidal properties of N-phosphonomethylglycine and its derivatives were first discovered by Franz, then disclosed and patented in U.S. Patent No. 3,799,758, issued March 26, 1974. A number of herbicidal salts of N-phosphonomethylglycine were patented by Franz in U.S. Patent No. 4,405,531, issued September 20, 1983. The disclosures of both of these patents are hereby incorporated by reference.

Various salts of N-phosphonomethylglycine are commercially significant, in part because they are water soluble. Many of the salts listed herein are highly water soluble, thereby allowing for highly concentrated solutions that can be diluted at the site of use. In accordance with the methods of this invention, as they pertain to glyphosate herbicide, a solution containing a herbicidally effective amount of glyphosate, and other components as described elsewhere herein (e.g., a pyridine analog, and optionally a surfactant), is applied to the foliage of plants.

A pyridine analog or derivative thereof (i.e., an acid, a salt or an ester form thereof), such as one or more of those disclosed in U.S. Patent No. 4,692,184 (which is incorporated in its entirety herein by reference for all relevant purposes), is another component of the composition of the present invention. In this regard it is to be noted that the phrase "pyridine analogs", as well as variations thereof, is intended to generally refer to a class of herbicides that includes, for example: triclopyr (i.e., [(3,5,6-trichloro-2-pyridinyl)oxylacetic acid), clopyralid (i.e., 3,6-dichloro-2-pyridine carboxylic acid), fluroxypyr (i.e., [(4-amino-3,5-dichoro-6-fluoro-pyridyl)oxylaetic acid), dithiopyr (i.e., S,S-dimethylester-2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridine dicarbothioic acid), thiazopyr (i.e., methyl 2-(difluoromethyl)-5-(4,5-dihydro-2-thiazolyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3pyridine carboxylate), and picloram (i.e., 4-amino-3,5,6-trichloropicolinic acid), as well as derivatives thereof, in all of their various forms, including for example the acid, the salt (e.g., amine salt, such as monoethanolamine or triethylamine), and the ester (e.g., butoxyethyl ester). Such compounds may be characterized, in one aspect of the present invention, by the rapid symptomology and more consistent control they impart.

In this regard it is to be noted that the present invention encompasses essentially any formulation disclosed herein (e.g., concentrate, solid or tank mix) which comprises glyphosate and any one of triclopyr, clopyralid, fluroxypyr, dithiopyr, thiazopyr, picloram, or a derivative thereof, as well as any combination or mixture

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which includes any one, two, there, four, five or six of these pyridine analogs. Exemplary co-herbicidal combinations are set forth in greater detail in Coherbicide Tables A-E, below (which illustrate that glyphosate, or one of its salts, can be combined with pyridine analog herbicides to form a herbicidal composition comprising two to seven actives, wherein: G = glyphosate; Tr = triclopyr; C = clopyralid; F = fluroxypyr; D = dithiopyr; Th = thiazopyr; P = picloram; and "Active No." is a herbicide combination reference number):

Table A: Glyphosate in combination with one pyridine analog herbicide

Active No.	Herbicides	Active No.	Herbicides
1	G + Tr	4	G + D
2	G+C	5	G + Th
3	G+F	6	G+P

Table B: Glyphosate in combination with two pyridine analog herbicides

Active No.	Herbicides	Active No.	Herbicides	Active No.	Herbicides
7	G + Tr + P	12	G+P+C	17	G + C + Th
8	G + Tr + C	13	G+P+D	18	G+C+F
9	G + Tr + D	14	G + P + Th	19	G + D + Th
10	G + Tr + Th	15	G+P+F	20	G+D+F
11	G + Tr + F	16	G+C+D	21	G + Th + F

## Table C: Glyphosate in combination with three pyridine analog herbicides

Active No.	Herbicides	Active No.	Herbicides
22	G + Tr + P + C	32	G+P+C+D
23	G + Tr + P + D	33	G + P + C + Th
24	G+Tr+P+Th	34	G+P+C+F
25	G + Tr + P + F	35	G + P + D + Th
26	G + Tr + C + D	36	G+P+D+F
27	G + Tr + C + Th	37	G + P + Th + F
28	G + Tr + C + F	38	G + C + D + Th
29	G + Tr + D + Th	39	G+C+D+F
30	G + Tr + D + F	40	G + C + Th + F
31	G + Tr + Th + F	41	G + D + Th + F

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Table D: Glyphosate in combination with four pyridine analog herbicides

Active No.	Herbicides	Active No.	Herbicides
42	G + Tr + P + C + D	50	G + Tr + C + Th + F
43	G + Tr + P + C + Th	51	G + Tr + D + Th + F
44	G + Tr + P + C + F	52	G + P + C + D + Th
45	G + Tr + P + D + Th	53	G+P+C+D+F
46	G + Tr + P + D + F	54	G + P + C + Th + F
47	G + Tr + P + Th + F	55	G + P + D + Th + F
48	G + Tr + C + D + Th	56	G + C + D + Th + F
49	G + Tr + C + D + F		

Table E: Glyphosate in combination with five pyridine analog herbicides

Active No.	Herbicides
57	G + Tr + P + C + D + Th
58	G + Tr + P + C + D + F
59	G + Tr + P + C + Th + F
60	G + Tr + P + D + Th + F
61	G + Tr + C + D + Th + F
62	G + P + C + D + Th + F

In one preferred embodiment, the pyridine analog is selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr, picloram, or some combination thereof. In an alternative preferred embodiment, the pyridine analog is selected from the group consisting of triclopyr, clopyralid, dithiopyr, thiazopyr, or some combination thereof. In yet another preferred embodiment, the pyridine analog is selected from the group consisting of triclopyr, clopyralid, dithiopyr, or some combination thereof. In yet another preferred embodiment, the pyridine analog is selected from the group consisting of triclopyr, clopyralid, or a combination thereof. In yet another preferred embodiment, the pyridine analog is selected from the group consisting of triclopyr, dithiopyr, thiazopyr, or some combination thereof. In yet another preferred embodiment, the pyridine analog is selected from the group consisting of triclopyr, clopyralid, fluroxypyr, or some combination thereof.

With respect to the ester and salt forms of the pyridine analogs or derivatives thereof of the present invention, it is to be noted that the present invention

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encompasses essentially any such ester or salt known to one of ordinary skill in the art, or which may be prepared thereby using techniques known in the art. Exemplary salts may include alkali metal salts, for example sodium and potassium salts, ammonium salts, alkylammonium salts (e.g.,  $C_{1-16}$  alkylammonium), alkanolammonium salts (e.g.,  $C_{1-16}$  alkanolammonium), di-ammonium salts such as dimethylammonium, alkylamine salts, for example dimethylamine and isopropylamine salts, alkanolamine salts, for example ethanolamine salts, alkylsulfonium salts (e.g.,  $C_{1-16}$  alkylsulfonium, for example trimethylsulfonium salts), sulfoxonium salts, and mixtures or combinations thereof.

#### B. Concentrations and Ratios

The relative amounts of glyphosate and the pyridine analog (e.g., triclopyr, clopyralid, fluroxypyr, dithiopyr, thiazopyr, picloram, etc., or a combination thereof) present in a contemplated herbicidal composition (i.e., a particulate solid concentrate, or liquid concentrate, or alternatively a ready-to-use, or tank-mix, composition) may vary depending upon many factors, including for example the plant species to be controlled and the method of application. Generally speaking, however, the concentrations of these herbicides, and optionally a surfactant and/or some other additive (as described elsewhere herein), in the herbicidal compositions of the invention is sufficient to provide at least about 70% control (as determined by means known in the art) within about 50 days, preferably about 40 days, more preferably about 30 days, still more preferably about 20 days, still more preferably about 15 days, still more preferably about 10 days, still more preferably about 5 days, and even still more preferably about 1 day, or less, after application of the composition to a plant. In a more preferred embodiment, the concentration of these herbicides, and optionally a surfactant and/or some other additive, in the herbidical compositions of the invention is sufficient to provide at least about 80%, more preferably at least about 85%, still more preferably at least about 90%, and still more preferably at least about 95%, control, or more, within about 50 days, preferably about 40 days, more preferably about 30 days, still more preferably about 20 days, still more preferably about 15 days, still more preferably about 10 days, still more preferably about 5 days, and even still more preferably about 1 day, or less, after application of the composition to a plant.

Additionally, the concentrations of these herbicides, and optionally a surfactant and/or some other additive (as described elsewhere herein), in the herbicidal compositions of the invention is sufficient to provide at least about 70% control of plant regrowth (as determined by means known in the art) for at least

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about 20, preferably at least about 30, more preferably at least about 40, still more preferably at least about 50, still more preferably at least about 60, still more preferably at least about 70, still more preferably at least about 80, or even still more preferably at least about 90, days after application of the composition to a plant. In a more preferred embodiment, the concentrations of these herbicides, and optionally a surfactant and/or some other additive, in the herbidical compositions of the invention is sufficient to provide at least about 80%, more preferably at least about 85%, still more preferably at least about 90%, or still more preferably at least about 95% control, or more, for at least about 20, more preferably at least about 30, still more preferably at least about 40, still more preferably at least about 50, still more preferably at least about 60, still more preferably at least about 70, still more preferably at least about 80, or even still more preferably at least about 90, days after application to the plant.

Accordingly, in some embodiments of the present invention (e.g., the concentrate herbicidal composition), the glyphosate concentration may be at least about 50 grams, preferably at least about 75 grams, more preferably at least about 100 grams, still more preferably at least about 125 grams, still more preferably at least about 150 grams, still more preferably at least about 175 grams, still more preferably at least about 220 grams, still more preferably at least about 225 grams, still more preferably at least about 250 grams, (acid equivalent) per liter, or more (e.g., at least about 300 grams, at least about 350 grams, at least about 400 grams, at least about 450 grams, at least about 500 grams, at least 550 grams, at least 600 grams per liter, or more). The glyphosate concentration may therefore range from, for example, about 50 to about 500 grams (a.e.) per liter, from about 100 to about 400 grams per liter, from about 150 to about 300 grams per liter, or from about 175 to about 250 grams per liter.

In an alternative embodiment, the concentration of glyphosate may be no greater than 165 grams per liter (e.g., no greater than 160 grams per liter, 155 grams per liter, 150 grams per liter, 140 grams per liter, or even no greater than about 130, about 120, about 110, about 100, about 75 grams per liter or less). The glyphosate concentration may therefore range, for example, from about 100 to no greater than 160 grams per liter, or from about 110 to no greater than 150 grams per liter.

In still other embodiments (e.g., a ready-to-use composition, also known and referred to herein as a tank mix composition), the glyphosate concentration may be less than about 50, preferably less than about 45, more preferably less than about 40, still more preferably less than about 35, still more preferably less than about 30, or even still more preferably less than about 25 grams (a.e.) per liter (e.g., about 2,

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about 4, about 6, about 8, about 10, about 12, about 14, about 16, about 18 or about 20 grams (a.e.) per liter). Accordingly, the glyphosate concentration may range, for example, from about 2 to about 50 grams (a.e.) per liter, from about 4 to about 25, from about 6 to about 15, or from about 8 to about 12 grams (a.e.) per liter. In some instances, such as wherein:

- (i) the weight ratio (a.e. to a.e.) of glyphosate to the pyridine analog is at least 4:1 (e.g., at least about 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 11:1, 12:1, 13:1, 14:1, 15:1, 20:1, 40:1, 60:1, 80:1, or even 100:1), the concentration of glyphosate may be no greater than 16.2 grams (a.e.) per liter (e.g., no greater than about 16, about 15.5, about 15, about 14.5, about 14, about 13.5, about 13, about 12.5, about 12, about 11.5, about 11, about 10.5, about 10, about 9.5, about 9, about 8.5, about 8, about 7.5, about 7, about 6.5, about 6, about 5.5, about 5, etc., the concentration thus ranging from, for example, about 5 to about 16, from about 7 to about 14, or from about 8 to about 12, grams (a.e.) per liter); exemplary combinations include a ratio of at least 4:1, about 8:1, or even about 10:1 with a glyphosate concentration of less than about 15 grams (a.e.) per liter, 12 grams (a.e.) per liter, 10 grams (a.e.) per liter, or even 8 grams (a.e.) per liter; and/or
- (ii) the weight ratio (a.e. to a.e.) of glyphosate to pyridine analog is at least 6:1 (e.g., at least about 7:1, 8:1, 9:1, 10:1, 11:1, 12:1, 13:1, 14:1, 15:1, 20:1, 40:1, 60:1, 80:1, or even 100:1), the concentration of glyphosate may be no greater than 23.8 grams (a.e.) per liter (e.g., no greater than about 23.5, about 23, about 22.5, about 22, about 21.5, about 21, about 20.5, about 20, about 19.5, about 19, about 18.5, about 18, about 17.5, about 17, about 16.5, about 16, about 15.5, about 15, about 14.5, about 14, about 13.5, about 13, about 12.5, about 12, about 11.5, about 11, about 10.5, about 10, about 9.5, about 9, about 8.5, about 8, about 7.5, about 7, about 6.5, about 6, about 5.5, about 5, etc., the concentration thus ranging from, for example, about 5 to about 22, from about 6 to about 20, or from about 8 to about 15, grams (a.e.) per liter); exemplary combinations include a ratio of at least 6:1, about 8:1, or even about 10:1 with a glyphosate concentration of less than about 20 grams (a.e.) per liter, 15 grams (a.e.) per liter, 12 grams (a.e.) per liter, 10 grams (a.e.) per liter, or even 8 grams (a.e.) per liter.

With respect to the glyphosate concentration, it is to be noted that as the concentration of glyphosate increases, the concentration of one or more other

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ingredients in the present composition may be reduced to maintain the solubility of one or more of the ingredients therein (i.e., to ensure these ingredients remain in solution).

The concentration of the pyridine analog in the herbicidal composition of the present invention may also vary. For example, the concentration may preferably be sufficient to provide visual symptoms of herbicide treatment within about 5 days, preferably about 4 days, or more preferably about 3 days after application of the composition to the plant, and in some instances may be sufficient to provide such symptoms within about 2 days, about 1 day or even less, after the application. However, in this regard it is to be noted that the concentration of the pyridine analog is also preferably controlled, such that it is not substantially antagonistic to the herbicidal activity of the glyphosate, or glyphosate derivative, within the composition.

Accordingly, in some embodiments of the present invention (e.g., the concentrate herbicidal composition), the concentration of the pyridine analog may be, for example, at least about 1, about 2, about 4, about 6, about 8, about 10, about 15, about 20, about 25, about 30, about 35, about 40, about 45, about 50, about 60, about 70, about 80, about 90, about 100 or more grams (a.e.) per liter. The concentration of the pyridine analog may therefore range, for example, from about 1 to about 99 or 100 grams (a.e.) per liter (e.g., about 1 to about 99 or 100, about 2 to about 80, about 4 to about 60, about 6 to about 40, or about 8 to about 20, grams (a.e.) per liter).

In these or other embodiments of the present invention, it is to be noted that the concentration may alternatively be not greater than 99 grams (a.e.) per liter (e.g., not greater than about 95, about 90, about 85, about 80, about 75, about 70, about 65, about 60, about 55, about 50, about 40, about 30, about 20, about 10, about 5 or less grams (a.e.) per liter). Accordingly, the concentration of the pyridine analog may range from, for example, about 1 to less than 99 grams (a.e.) per liter (e.g., from about 2 to less than about 80, from about 4 to less than about 60, from about 6 to less than about 40, or from about 8 to less than about 20, grams (a.e.) per liter).

In still other embodiments (e.g., a ready-to-use composition), the concentration of the pyridine analog may be less than about 25, about 15 or even about 10 grams (a.e.) liter, the concentration ranging for example from about 0.2 to about 10 grams (a.e.) per liter, from about 0.4 to about 6, from about 0.6 to about 4, or from about 0.8 to about 2 grams (a.e.) per liter. Additionally, or alternatively, the concentration of the pyridine analog may be not greater than 3.9 grams (a.e.) per liter (e.g., not greater than about 3.8, about 3.7, about 3.6, about 3.5, about 3.4, about 3.3, about 3.2, about 3.1, about 3, about 2.8, about 2.6, about 2.4, about 2.2, about 2, about 1.8, about 1.6, about 1.4, about 1.2, about 1, about 0.8, about 0.6,

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about 0.4, about 0.2 grams (a.e.) per liter or less, the concentration ranging for example from about 0.2 to about 3.5 grams (a.e.) per liter, from about 0.4 to about 3, from about 0.6 to about 2.5, or from about 0.8 to about 2 grams (a.e.) per liter).

With respect to the weight ratio (a.e. to a.e.) of glyphosate to the pyridine analog, generally speaking this is greater than about 1:1 (i.e., glyphosate is in excess); that is, this ratio may be at least about 1.1:1, about 1.2:1, about 1.3:1, about 1.4:1, about 1.5:1, about 1.6:1, about 1.7:1, about 1.8:1, about 1.9:1, about 2:1, about 2.2:1, about 2.4:1, about 2.6:1, about 2.8:1, about 3:1, about 4:1, about 5:1, about 6:1, about 7:1, about 8:1, about 9:1, about 10:1, about 11:1, about 12:1, about 13:1, about 14:1, about 15:1, about 20:1, about 25:1, about 30:1, about 35:1, about 40:1, about 45:1, about 50:1 or more (e.g., about 60:1, about 70:1, about 80:1, about 90:1 or even about 100:1). Accordingly, this ratio may range from about 1:1 to about 100:1, from about 2:1 to about 80:1, from about 4:1 to about 60:1, from about 6:1 to about 40:1, or from about 8:1 to about 20:1.

Alternatively, in some embodiments (e.g., a ready-to-use composition), this ratio may be at least 7.6:1, and preferably may be at least about 7.7:1, about 7.8:1, about 7.9:1, about 8:1, about 8.2:1, about 8.4:1, about 8.6:1, about 8.8:1, about 9:1, about 9.2:1, about 9.4:1, about 9.6:1, about 9.8:1, about 10:1 or more (e.g., about 11:1, about 12:1, about 13:1, about 14:1, about 15:1, about 20:1, about 25:1, about 30:1, about 35:1, about 40:1, about 45:1, about 50:1, about 60:1, about 70:1, about 80:1, about 90:1 or even about 100:1). Accordingly, this ratio ranges from, for example, about 7.8:1 to about 20:1, from about 8:1 to about 15:1, from about 8.4:1 to about 14:1, or about 9:1 to about 12:1.

Additionally, in yet other alternative embodiments (e.g., concentrate or ready-to-use compositions), wherein for example picloram is used, the ratio of glyphosate to pyridine analog (e.g., picloram) may be greater than about 1:1 and less than about 32:1, range for example from about 5:1 to about 30:1, from about 10:1 to about 25:1, from about 11:1 to about 20:1, from about 12:1 to about 18:1, or from about 14:1 to about 16:1.

In view of the foregoing, and as further described elsewhere herein, it is to be noted that the concentration of glyphosate, the concentration of the pyridine analog (e.g., triclopyr, clopyralid, fluroxypyr, dithiopyr, thiazopyr, picloram, etc., or a combination thereof), the weight ratio of glyphosate to the pyridine analog, and/or the various ranges associated therewith, may be other than herein described without departing from the scope of the present invention.

It is to be further noted that the various concentrations of the pyridine analog provided herein, as well as the various ratios of glyphosate to the pyridine analog, are intended to apply indepedently to each analog; that is, although not specifically

recited, it is to be noted that each concentration, concentration range, ratio, etc. noted herein is intended to apply independently triclopyr, clopyralid, fluroxypyr, dithiopyr, thiazopyr, picloram, etc., or a combination thereof.

#### II. Surfactants

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Various surfactants may be effective in formulating the herbicidal compositions or concentrates of the present invention, including for example the nonionic, cationic, anionic and amphoteric surfactants as described below, as well as mixtures thereof.

Cationic surfactants effective in such glyphosate compositions or formulations include, for example:

(a) a secondary or tertiary amine having the formula:

$$R^1 \longrightarrow N \stackrel{}{\underset{}{\stackrel{}}} R^2$$

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wherein R¹ and R² are hydrocarbyl having from 1 to about 30 carbon atoms, and R³ is hydrogen or hydrocarbyl having from 1 to about 30 carbon atoms. In this context, preferred R¹, R², and R³ hydrocarbyl groups are linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl groups. Preferably, R¹ is a linear or branched alkyl or linear or branched alkenyl group having from about 8 to about 30 carbon atoms, and R² and R³ are independently hydrogen or a linear or branched alkyl or linear or branched alkenyl group having from 1 to about 6 carbon atoms. More preferably, R¹ is a linear or branched alkyl group having from about 12 to about 22 carbon atoms, and R² and R³ are independently hydrogen, methyl, ethyl, or linear or branched hydroxyalkyl groups having from 1 to about 6 carbon atoms.

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In an alternative embodiment, the surfactant may have the formula (1) wherein R¹ is hydrocarbyl or substituted hydrocarbyl having from about 8 to about 30 carbon atoms, R² is a hydroxyalkyl, polyhydroxyalkyl or poly(hydroxyalkyl)alkyl group, and R³ is hydrogen, hydroxyalkyl, polyhydroxyalkyl or poly(hydroxyalkyl)alkyl. In this context, preferred R¹ hydrocarbyl groups are linear or branched alkyl, linear or branched alkynyl, aryl, or aralkyl groups. In one embodiment, R¹ is a linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl group having from about 8 to about 30 carbon atoms, R² is a linear or branched hydroxyalkyl group having from 1 to about 6 carbon atoms, and R³ is hydrogen or a linear or branched hydroxyalkyl group having

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from 1 to about 6 carbon atoms. Preferably, R¹ is a linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl group having from about 8 to about 22 carbon atoms, R² is a linear or branched hydroxyalkyl group having from 1 to about 4 carbon atoms, and R³ is hydrogen or a linear or branched hydroxyalkyl group having from 1 to about 4 carbon atoms. More preferably, R¹ is a linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl group having from about 8 to about 18 carbon atoms, R² is hydroxymethyl or hydroxyethyl, and R³ is hydrogen, hydroxymethyl or hydroxyethyl.

(b) a monoalkoxylated amine having the formula:

$$R^{1} - N_{R^{4}}^{(R^{2}O)_{x}R^{3}}$$
 (2)

wherein R<sup>1</sup> and R<sup>4</sup> are independently hydrocarbyl or substituted hydrocarbyl groups having from 1 to about 30 carbon atoms or -R<sup>5</sup>SR<sup>6</sup>, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene, R<sup>3</sup> is hydrogen, or a linear or branched alkyl group having from 1 to about 4 carbon atoms, R<sup>5</sup> is a linear or branched alkyl group having from about 6 to about 30 carbon atoms, R<sup>6</sup> is a hydrocarbyl or substituted hydrocarbyl group having from 4 to about 15 carbon atoms and x is an average number from 1 to about 60. In this context, preferred R<sup>1</sup>, R<sup>4</sup>, and R<sup>6</sup> hydrocarbyl groups are linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl groups. In one embodiment, R1 includes from about 7 to about 30 carbon atoms, preferably from about 8 to about 22 carbon atoms, and the remaining groups are as described above. Preferably, R<sup>1</sup> and R<sup>4</sup> are independently a linear or branched alkyl or linear or branched alkenyl group having from 1 to about 25 carbon atoms. R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene,  $R^3$  is hydrogen, methyl or ethyl, and x is an average number from 1 to about 40. More preferably, R<sup>1</sup> and R<sup>4</sup> are independently a linear or branched alkyl group having from 1 to about 22 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, and x is an average number from 1 to about 30. Even more preferably, R<sup>1</sup> is a linear or branched alkyl group having from about 8 to about 22 carbon atoms and R4 is a linear or branched alkyl group having from 1 to about 22 carbon atoms, R2 in each of the x (R2O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, and x is an average number from about 1 to about 10. Most preferably, R1 is a linear or branched alkyl group having from about 16 to about 22 carbon atoms and R4 is methyl, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is ethylene, R<sup>3</sup> is hydrogen, and x is an average number from about 1 to about 5, or R1 is a linear or branched alkyl group

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having from about 8 to about 15 carbon atoms and  $R^4$  is methyl,  $R^2$  in each of the x ( $R^2O$ ) groups is ethylene,  $R^3$  is hydrogen, and x is an average number from about 5 to about 10.

(c) a dialkoxylated quaternary ammonium salt having the formula:

$$\begin{array}{c|c}
(R^{2}O)_{x}R^{3} & X^{-} \\
R^{1} & N^{+} & (R^{2}O)_{y}R^{3} \\
R^{4} & (3)
\end{array}$$

wherein R<sup>1</sup> is hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms,  $R^2$  in each of the x ( $R^2O$ ) and y ( $R^2O$ ) groups is independently  $C_2$ - $C_4$ alkylene, R³ is hydrogen, or a linear or branched alkyl group having from 1 to about 4 carbon atoms, R4 is hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, x and y are independently an average number from 1 to about 40, and X- is an agriculturally acceptable anion. In this context, preferred R1 and R4 hydrocarbyl groups are linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl groups. Preferably, R1 and R<sup>4</sup> are independently a linear or branched alkyl or linear or branched alkenyl group having from 1 to about 25 carbon atoms, R2 in each of the x (R2O) and y (R2O) groups is independently C2-C4 alkylene, R3 is hydrogen, methyl or ethyl, and the sum of x and y is an average number from about 2 to about 30. More preferably, R<sup>1</sup> and R4 are independently a linear or branched alkyl group having from 1 to about 22 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) and y (R<sup>2</sup>O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, and the sum of x and y is an average number from about 2 to about 20. Even more preferably, R<sup>1</sup> is a linear or branched alkyl group having from about 8 to about 22 carbon atoms and R4 is a linear or branched alkyl group having from 1 to about 22 carbon atoms, R2 in each of the x (R<sup>2</sup>O) and y (R<sup>2</sup>O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, and the sum of x and y is an average number from about 2 to about 20. Most preferably, R1 is a linear or branched alkyl group having from about 8 to about 22 carbon atoms and R4 is a linear or branched alkyl group having from 1 to about 6 carbon atoms, R2 in each of the x (R2O) and y (R2O) groups is independently ethylene or propylene, R3 is hydrogen or methyl, and the sum of x and y is an average number from about 2 to about 15, or R<sup>1</sup> and R<sup>4</sup> are independently a linear or branched alkyl group having from about 8 to about 22 carbon atoms, R2 in each of the x (R<sup>2</sup>O) and y (R<sup>2</sup>O) groups is independently ethylene or propylene, R<sup>3</sup> is

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hydrogen or methyl, and the sum of x and y is an average number from about 5 to about 15. Preferred dialkoxylated quaternary ammonium surfactants include Ethoquad™ C12 (a PEG 2 coco methyl ammonium chloride from Akzo Nobel), PEG 5 coco methyl ammonium chloride, PEG 5 tallow methyl ammonium chloride, PEG 5 ditallow ammonium bromide, and PEG 10 ditallow ammonium bromide.

(d) a monoalkoxylated quaternary ammonium salt having the formula:

$$\begin{array}{c|c}
R^{5} & X^{-} \\
R^{1} & N^{+} & (R^{2}O)_{x}R^{3} \\
R^{4} & R^{4}
\end{array}$$

(4)

wherein R<sup>1</sup> and R<sup>5</sup> are independently hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, R<sup>4</sup> is hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently C2-C4 alkylene, R3 is hydrogen, or a linear or branched alkyl group having from 1 to about 30 carbon atoms, x is an average number from 1 to about 60, and X- is an agriculturally acceptable anion. In this context, preferred R<sup>1</sup>, R<sup>4</sup>, and R<sup>5</sup> hydrocarbyl groups are linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl groups. Preferably, R1, R4 and R5 are independently a linear or branched alkyl or linear or branched alkenyl group having from 1 to about 25 carbon atoms, R2 in each of the x (R2O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene, R<sup>3</sup> is hydrogen, methyl or ethyl, and x is an average number from 1 to about 40. More preferably, R<sup>1</sup>, R<sup>4</sup> and R<sup>5</sup> are independently a linear or branched alkyl group having from 1 to about 22 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, and x is an average number from 1 to about 30. Even more preferably, R1 is a linear or branched alkyl group having from about 8 to about 22 carbon atoms, R2 in each of the x (R<sup>2</sup>O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, R<sup>4</sup> and R<sup>5</sup> are independently a linear or branched alkyl group having from 1 to about 22 carbon atoms, and x is an average number from 1 to about 30. Even more preferably, R1 is a linear or branched alkyl group having from about 8 to about 22 carbon atoms, R2 in each of the x (R2O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, R<sup>4</sup> and R<sup>5</sup> are independently a linear or branched alkyl group having from 1 to about 6 carbon atoms, and x is an average number from about 5 to about 25. Most preferably, R1 is a linear or branched alkyl group having from about 16 to about 22 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O)

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groups is independently ethylene or propylene,  $R^3$  is hydrogen or methyl,  $R^4$  and  $R^5$  are independently a linear or branched alkyl group having from 1 to about 3 carbon atoms, and x is an average number from about 5 to about 25. Preferred monoalkoxylated quaternary ammonium surfactants include PEG 7  $C_{18}$  dimethyl ammonium chloride and PEG 22  $C_{18}$  dimethyl ammonium chloride.

(e) a quaternary ammonium salt having the formula:

wherein R1, R3 and R4 are independently hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, R<sup>2</sup> is hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, and X- is an agriculturally acceptable anion. In this context, preferred R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> hydrocarbyl groups are linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl groups. Preferably, R1 is a linear or branched alkyl or linear or branched alkenyl group having from about 8 to about 30 carbon atoms, and R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently a linear or branched alkyl or linear or branched alkenyl group having from 1 to about 30 carbon atoms. More preferably, R<sup>1</sup> is a linear or branched alkyl or linear or branched alkenyl group having from about 8 to about 22 carbon atoms, and R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently a linear or branched alkyl or linear or branched alkenyl group having from 1 to about 6 carbon atoms. Even more preferably, R1 is a linear or branched alkyl group having from about 8 to about 16 carbon atoms, and R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently a linear or branched alkyl group having from 1 to about 6 carbon atoms. Most preferably, R<sup>1</sup> is a linear or branched alkyl group having from about 8 to about 14 carbon atoms, and R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are methyl. Preferred commercially available quaternary ammonium surfactants include Arquad™ C-50 (a dodecyl trimethyl ammonium chloride from Akzo Nobel) and Arquad™ T-50 (a tallow trimethyl ammonium chloride from Akzo Nobel).

(f) an ether amine having the formula:

$$R^{1}O - R^{2} - N$$
 $R^{4}$ 
(6)

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wherein R<sup>1</sup> is hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms; R<sup>2</sup> is hydrocarbylene or substituted hydrocarbylene having from 2 to about 30 carbon atoms; R<sup>3</sup> and R<sup>4</sup> are independently hydrogen, hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, or -(R<sup>5</sup>O)<sub>x</sub>R<sup>6</sup>, R<sup>5</sup> in each of the x(R5-O) groups is independently C2-C4 alkylene, R6 is hydrogen, or a linear or branched alkyl group having from 1 to about 4 carbon atoms, and x is an average number from 1 to about 50. In this context, preferred R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> hydrocarbyl (hydrocarbylene) groups are linear or branched alkyl (alkylene), linear or branched alkenyl (alkenylene), linear or branched alkynyl (alkynylene), aryl (arylene), or aralkyl (aralkylene) groups. Preferably, R<sup>1</sup> is a linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl group having from 8 to about 25 carbon atoms, R<sup>2</sup> is a linear or branched alkylene or alkenylene group having from 2 to about 30 carbon atoms, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen, a linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl group having from 1 to about 30 carbon atoms, or -(R<sup>5</sup>O), R<sup>6</sup>, R<sup>5</sup> in each of the x (R<sup>5</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene, R<sup>6</sup> is hydrogen, methyl or ethyl, and x is an average number from 1 to about 30. More preferably, R<sup>1</sup> is a linear or branched alkyl or alkenyl group having from 8 to about 22 carbon atoms, R<sup>2</sup> is a linear or branched alkylene or alkenylene group having from 2 to about 6 carbon atoms, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen, a linear or branched alkyl or alkenyl group having from 1 to about 6 carbon atoms, or -(R<sup>5</sup>O), R<sup>6</sup>, R<sup>5</sup> in each of the x (R<sup>5</sup>O) groups is independently ethylene or propylene, R<sup>6</sup> is hydrogen or methyl, and x is an average number from 1 to about 15. Most preferably, R1 is a linear or branched alkyl or alkenyl group having from 8 to about 18 carbon atoms, R2 is ethylene or propylene, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen, methyl, or -(R<sup>5</sup>O), R<sup>6</sup>, R<sup>5</sup> in each of the x (R<sup>5</sup> O) groups is independently ethylene or propylene, R<sup>6</sup> is hydrogen, and x is an average number from 1 to about 5.

(q) a diamine having the formula:

$$R^{1}_{-}(X)_{z}-(R^{8})_{\overline{n}} - NH_{-}_{-}(R^{6}O)_{y-}R^{2}_{-}N^{-}R^{3}$$
 $R^{4}$ 
 $R^{5}$ 
(7)

wherein  $R^1$ ,  $R^3$ ,  $R^4$  and  $R^5$  are independently hydrogen, hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, or  $-(R^6O)_xR^7$ ;  $R^2$  and  $R^8$  are independently hydrocarbylene or substituted hydrocarbylene having from 2 to about 30 carbon atoms,  $R^6$  in each of the x ( $R^6O$ ) and y ( $R^6O$ ) groups is independently  $C_2$ - $C_4$  alkylene,  $R^7$  is hydrogen, or a linear or branched alkyl group having from 1 to

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about 30 carbon atoms, x is an average number from 1 to about 30, X is -O-,  $-N(R^6)$ -, -C(O)-, -C(O)O-, -OC(O)-,  $-N(R^9)C(O)$ -,  $-C(O)N(R^9)$ -, -S-, -SO-, or -SO<sub>2</sub>-, y is 0 or an average number from 1 to about 30, n and z are independently 0 or 1, and R<sup>9</sup> is hydrogen or hydrocarbyl or substituted hydrocarbyl. In this context, preferred R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>9</sup> hydrocarbyl (hydrocarbylene) groups are linear or branched alkyl (alkylene), linear or branched alkenyl (alkenylene), linear or branched alkynyl (alkynylene), aryl (arylene), or aralkyl (aralkylene) groups. Preferably, R1 and R4 are independently a linear or branched alkyl or linear or branched alkenyl group having from about 1 to about 22 carbon atoms, R<sup>2</sup> and R<sup>8</sup> are independently linear or branched alkylene groups having from about 2 to about 25 carbon atoms, R3 and R5 are each independently hydrogen or a linear or branched alkyl group having from 1 to about 6 carbon atoms and n, y and z are 0; or R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or a linear or branched alkyl or alkenyl group having from about 1 to about 6 carbon atoms, R<sup>2</sup> is a linear or branched alkylene or alkenylene group having from about 8 to about 25 carbon atoms, and n, y and z are 0; or R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or a linear or branched alkyl or alkenyl group having from about 1 to about 6 carbon atoms, R2 is a linear or branched alkylene or alkenylene group having from about 1 to about 6 carbon atoms, R<sup>6</sup> in each of the y (R<sup>6</sup>O) groups is independently C2-C4 alkylene, y is an average number from 1 to about 20 and n and z are 0; or R<sup>1</sup> and R<sup>3</sup> are independently a linear or branched alkyl or linear or branched alkenyl group having from about 8 to about 22 carbon atoms. R<sup>2</sup> is a linear or branched alkylene group having from about 2 to about 25 carbon atoms; and R<sup>4</sup> and R<sup>5</sup> are each independently hydrogen, a linear or branched alkyl or alkenyl group having from 1 to about 6 carbon atoms, or -(R<sup>6</sup>O), R<sup>7</sup>, R<sup>6</sup> in each of the x (R<sup>6</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene, R<sup>7</sup> is hydrogen, or a linear or branched alkyl group having from 1 to about 4 carbon atoms, x is an average number from 1 to about 30, and n, y and z are 0; or R<sup>1</sup> is a linear or branched alkyl or linear or branched alkenyl group having from about 1 to about 22 carbon atoms, R<sup>2</sup> is a linear or branched alkylene group having from about 2 to about 25 carbon atoms, R3, R4 and R5 are each independently hydrogen or a linear or branched alkyl group having from 1 to about 6 carbon atoms, X is -C(O)- or -SO<sub>2</sub>-, n and y are 0 and z is 1. More preferably, R1 and R4 are independently a linear or branched alkyl or linear or branched alkenyl group having from about 4 to about 18 carbon atoms, R<sup>2</sup> is a linear or branched alkylene group having from about 2 to about 6 carbon atoms, R<sup>3</sup> and R<sup>5</sup> are each independently hydrogen or a linear or branched alkyl group having from 1 to about 6 carbon atoms, and n, y and z are 0; or R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently hydrogen or a linear or branched alkyl group having from about 1 to about 6 carbon atoms, R<sup>2</sup> is a linear or branched alkylene group having from

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about 8 to about 25 carbon atoms, and y is 0; or R1, R2, R3 and R4 are independently hydrogen or a linear or branched alkyl group having from about 1 to about 6 carbon atoms, R<sup>2</sup> is a linear or branched alkylene group having from about 1 to about 6 carbon atoms, R<sup>6</sup> in each of the y (R<sup>6</sup>O) groups is independently ethylene or propylene, y is an average number from 1 to about 10 and n and z is 0; or R<sup>1</sup> and R<sup>3</sup> are independently a linear or branched alkyl group having from about 8 to about 22 carbon atoms, R<sup>2</sup> is a linear or branched alkylene group having from about 2 to about 6 carbon atoms, and R<sup>4</sup> and R<sup>5</sup> are each independently hydrogen, a linear or branched alkyl group having from 1 to about 6 carbon atoms, or -(R<sup>6</sup>O), R<sup>7</sup>, R<sup>6</sup> in each of the x (R<sup>6</sup>O) groups is independently ethylene or propylene, R<sup>7</sup> is hydrogen or methyl, x is an average number from 1 to about 15, and n, y and z are 0; or R<sup>1</sup> is a linear or branched alkyl group having from about 1 to about 22 carbon atoms. R<sup>2</sup> is a linear or branched alkylene group having from about 2 to about 6 carbon atoms, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each independently hydrogen, X is -C(O)- or -SO<sub>2</sub>-, n and y are 0 and z is 1. Preferred diamines include Gemini 14-2-14, Gemini 14-3-14, Gemini 10-2-10, Gemini 10-3-10, Gemini 10-4-10, and Gemini 16-2-16 (C<sub>10</sub>, C<sub>14</sub> or C<sub>16</sub> ethylene, propylene or butylene N-methyl diamines from Monsanto), Ethoduomeens™, and Jeffamine™ EDR-148.

# (h) an amine oxide having the formula:

$$R^{1} \xrightarrow{N+} R^{3}$$

$$R^{2}$$

(8)

wherein  $R^1$ ,  $R^2$  and  $R^3$  are independently hydrogen, hydrocarbyl or substituted hydrocarbyl,  $-(R^4O)_xR^5$ , or  $-R^6(OR^4)_xOR^5$ ;  $R^4$  in each of the x ( $R^4O$ ) groups is independently  $C_2$ - $C_4$  alkylene,  $R^5$  is hydrogen, or a linear or branched alkyl group having from 1 to about 30 carbon atoms,  $R^6$  is hydrocarbylene or substituted hydrocarbylene having from 2 to about 6 carbon atoms, x in each of the x ( $R^4O$ ) groups is independently an average number from 1 to about 50, and the total number of carbon atoms in  $R^1$ ,  $R^2$  and  $R^3$  is at least 8. In this context, preferred  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^6$  hydrocarbyl (hydrocarbylene) groups are linear or branched alkyl (alkylene), linear or branched alkenyl (alkenylene), linear or branched alkynyl (alkynylene), aryl (arylene), or aralkyl (aralkylene) groups. Preferably,  $R^1$  and  $R^2$  are independently hydrogen, a linear or branched alkyl or linear or branched alkenyl group having from 1 to about 30 carbon atoms, or  $-(R^4O)_xR^5$ ;  $R^3$  is a linear or branched alkyl or linear or branched alkenyl group having from about 8 to about 30

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carbon atoms,  $R^4$  in each of the x ( $R^4O$ ) groups is independently  $C_2$ - $C_4$  alkylene;  $R^5$  is hydrogen, methyl or ethyl, and x is an average number from 1 to about 30. More preferably,  $R^1$  and  $R^2$  are independently hydrogen, or a linear or branched alkyl group having from 1 to about 6 carbon atoms, and  $R^3$  is a linear or branched alkyl group having from about 8 to about 22 carbon atoms; or  $R^1$  and  $R^2$  are independently -( $R^4O$ )<sub>x</sub> $R^5$ ,  $R^3$  is a linear or branched alkyl group having from about 8 to about 22 carbon atoms,  $R^4$  in each of the x ( $R^4O$ ) groups is ethylene or propylene,  $R^5$  is hydrogen or methyl, and x is an average number from 1 to about 10. Most preferably,  $R^1$  and  $R^2$  are independently methyl, and  $R^3$  is a linear or branched alkyl group having from about 8 to about 18 carbon atoms; or  $R^1$  and  $R^2$  are independently -( $R^4O$ )<sub>x</sub> $R^5$ ,  $R^3$  is a linear or branched alkyl group having from about 8 to about 18 carbon atoms; or  $R^1$  and  $R^2$  are independently -( $R^4O$ )<sub>x</sub> $R^5$ ,  $R^3$  is a linear or branched alkyl group having from about 8 to about 18 carbon atoms,  $R^4$  in each of the x ( $R^4O$ ) groups is ethylene or propylene,  $R^5$  is hydrogen, and x is an average number from 1 to about 5. Commercially available amine oxide surfactants include Chemoxide L70.

(i) a dialkoxylated amine having the formula:

$$R^{1} - \sqrt{\frac{(R^{2}O)_{x}R^{3}}{(R^{2}O)_{y}R^{3}}}$$

(9)

wherein R<sup>1</sup> is a hydrocarbyl or substituted hydrocarbyl having from about 6 to about 30 carbon atoms, or -R<sup>4</sup>SR<sup>5</sup>, R<sup>4</sup> and R<sup>2</sup> in each of the x (R<sup>2</sup>O) and the y (R<sup>2</sup>O) groups is independently C2-C4 alkylene, R3 is hydrogen, or a linear or branched alkyl group having from 1 to about 4 carbon atoms, R<sup>5</sup> is a linear or branched alkyl group having from about 4 to about 15 carbon atoms, and x and y are independently an average number from 1 to about 40. In this context, preferred R1 hydrocarbyl groups are linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl groups. Preferably, R1 is a linear or branched alkynyl, aryl, or aralkyl group having from about 8 to about 30 carbon atoms, R2 in each of the x (R2O) and the y (R<sup>2</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene, R<sup>3</sup> is hydrogen, methyl or ethyl, and x and y are independently an average number from 1 to about 20. More preferably, R1 is a linear or branched alkynyl, aryl, or aralkyl group having from about 8 to about 25 carbon atoms, R2 in each of the x (R2O) and the y (R2O) groups is independently ethylene or propylene, R3 is hydrogen or methyl, and x and y are independently an average number from 1 to about 30. Even more preferably, R1 is a linear or branched alkynyl, aryl, or aralkyl group having from about 8 to about 22, or about 12 to about 22, carbon atoms, R2 in each of the x (R2O) and the y (R2O) groups is independently ethylene or propylene, R3 is hydrogen or methyl, and x and

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y are independently an average number from 1 to about 5. Some commercially available dialkoxylated amines include, for example, Trymeen<sup>™</sup> 6617 (from Cognis) and Ethomeen<sup>™</sup> C/12, C/15, C/20, C/25, T/12, T/15, T/20 and T/25 (from Akzo Nobel).

and (j) an aminated alkoxylated alcohol having the formula:

$$R^{1}$$
— $X$ — $(R^{2})_{m}$ — $(R^{3}O)_{n}$ — $R^{4}$ — $(NR^{6})_{q}$ — $N$ 
 $R^{8}$ 
(10)

wherein R<sup>1</sup>, R<sup>7</sup>, R<sup>8</sup>, and R<sup>9</sup> are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, or -(R<sup>11</sup>)<sub>s</sub>(R<sup>3</sup>O)<sub>v</sub>R<sup>10</sup>; X is -O-, -OC(O)-, -C(O)O-, -N(R<sup>12</sup>)C(O)-, -C(O)N(R<sup>12</sup>)-, -S-, -SO-, -SO<sub>2</sub>- or -N(R<sup>9</sup>)-; R<sup>3</sup> in each of the n (R<sup>3</sup>O) groups and the v (R<sup>3</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene; R<sup>10</sup> is hydrogen, or a linear or branched alkyl group having from 1 to about 30 carbon atoms; n is an average number from 1 to about 60; v is an average number from 1 to about 50; R<sup>2</sup> and R<sup>11</sup> are each independently hydrocarbylene or substituted hydrocarbylene having from 1 to about 6 carbon atoms; R4 is hydrocarbylene or substituted hydrocarbylene having from 2 to about 6 carbon atoms; R12 is hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms; m and s are each independently 0 or 1; R<sup>6</sup> is hydrocarbylene or substituted hydrocarbylene having from 2 to about 30 carbon atoms, -C(=NR<sup>12</sup>)-, -C(S)-, or -C(O)-; q is an integer from 0 to 5; and R<sup>5</sup> is hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms. In this context, preferred R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>11</sup> and R<sup>12</sup> hydrocarbyl (hydrocarbylene) groups are linear or branched alkyl (alkylene), linear or branched alkenyl (alkenylene), linear or branched alkynyl (alkynylene), aryl (arylene), or aralkyl (aralkylene) groups.

A subclass of such cationic surfactants includes monoalkoxylated amines having the formula:

$$R^{1}O - (R^{2}O)_{\overline{x}} - R^{3} - N R^{5}$$
(11)

wherein  $R^1$  is hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms;  $R^2$  in each of the x ( $R^2O$ ) and y ( $R^2O$ ) groups is

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independently C2-C4 alkylene; R3 is hydrocarbylene or substituted hydrocarbylene having from 2 to about 30 carbon atoms; R<sup>4</sup> and R<sup>5</sup> are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, -(R<sup>6</sup>)<sub>0</sub>-(R<sup>2</sup>O)<sub>v</sub>R<sup>7</sup>, or R<sup>4</sup> and R<sup>5</sup>, together with the nitrogen atom to which they are attached, form a cyclic or heterocyclic ring; R<sup>6</sup> is hydrocarbylene or substituted hydrocarbylene having from 1 to about 30 carbon atoms; R<sup>7</sup> is hydrogen or a linear or branched alkyl group having 1 to about 4 carbon atoms, n is 0 or 1, x and y are independently an average number from 1 to about 60. In this context, preferred R1, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> hydrocarbyl (hydrocarbylene) groups are linear or branched alkyl (alkylene), linear or branched alkenyl (alkenylene), linear or branched alkynyl (alkynylene), aryl (arylene), or aralkyl (aralkylene) groups. Preferably, R<sup>1</sup> is a linear or branched alkyl or linear or branched alkenyl group having from about 8 to about 25 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene, R<sup>3</sup> is a linear or branched alkylene group having from 2 to about 20 carbon atoms, R<sup>4</sup> and R<sup>5</sup> are each independently hydrogen or a linear or branched alkyl group having from 1 to about 6 carbon atoms, and x is an average number from 1 to about 30. More preferably, R<sup>1</sup> is a linear or branched alkyl group having from about 12 to about 22 carbon atoms, R2 in each of the x (R2O) groups is independently ethylene or propylene, R3 is a linear or branched alkylene group having from 2 to about 6 carbon atoms, R<sup>4</sup> and R<sup>5</sup> are each independently hydrogen, methyl, or tris(hydroxymethyl)methyl, and x is an average number from about 2 to about 30. Even more preferably, R1 is a linear or branched alkyl group having from about 12 to about 18 carbon atoms, R2 in each of the x (R2O) groups is independently ethylene or propylene, R3 is ethylene or propylene, R4 and R5 are each independently hydrogen, methyl or tris(hydroxymethyl)methyl, and x is an average number from about 4 to about 20. Most preferably, R1 is a linear or branched alkyl group having from about 12 to about 18 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently ethylene or propylene, R3 is ethylene, R4 and R5 are methyl, and x is an average number from about 4 to about 20. Preferred monoalkoxylated amines include PEG 13 or 18 C<sub>14-15</sub> ether propylamines and PEG 7, 10, 15 or 20 C<sub>16-18</sub> ether propylamines (from Tomah) and PEG 13 or 18 C<sub>14-15</sub> ether dimethyl propylamines and PEG 10, 15 or 20 or 25 C<sub>16-18</sub> ether dimethyl propylamines (from Tomah) and Surfonic™ AGM-550 from Huntsman.

Quaternary ammonium, sulfonium and sulfoxonium salts are also effective cationic surfactants in forming glyphosate concentrates and have the chemical structures:

$$R^{1}$$
— $X$ — $(R^{2})_{m}$ — $(R^{3}O)_{n}$ — $R^{4}$ — $(NR^{6})_{q}$ — $N^{+}$ — $R^{8}$   $A^{-}$ 

$$(12)$$

or

or

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$$A^{-}$$
  $R^{10}$   $R^{10}$ 

or

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$$R^{1} - S + - (R^{2})_{\overline{m}} (R^{3}O)_{\overline{n}} - R^{4} - (NR^{6})_{q} - N + - R^{8} A^{-}$$

(15)

wherein R<sup>1</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup> and R<sup>11</sup> are independently hydrogen, hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, or -(R<sup>13</sup>)<sub>s</sub>(R<sup>3</sup>O)<sub>v</sub>R<sup>12</sup>; X is -O-, -OC(O)-, -N(R<sup>14</sup>)C(O)-, -C(O)N(R<sup>14</sup>)-, -C(O)O-, or -S-; R<sup>3</sup> in each of the n (R<sup>3</sup>O) groups and v (R<sup>3</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene; R<sup>12</sup> is hydrogen, or a linear or branched alkyl group having from 1 to about 30 carbon atoms; n is an average number from 1 to about 50; R<sup>2</sup> and R<sup>13</sup> are each independently hydrocarbylene or substituted hydrocarbylene

having from 1 to about 6 carbon atoms; m and s are each independently 0 or 1; R<sup>4</sup> is hydrocarbylene or substituted hydrocarbylene having from 2 to about 6 carbon atoms; R<sup>6</sup> is hydrocarbylene or substituted hydrocarbylene having from 2 to about 30 carbon atoms, -C(=NR<sup>12</sup>)-, -C(S)-, or -C(O)-; R<sup>14</sup> is hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, q is an integer from 0 to 5; R<sup>5</sup> is hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms; and each A is an agriculturally acceptable anion. In this context, preferred R<sup>1</sup>, R<sup>2</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, R<sup>13</sup>, and R<sup>14</sup> hydrocarbyl (hydrocarbylene) groups are linear or branched alkyl (alkylene), linear or branched alkenyl (alkenylene), linear or branched alkynyl (alkynylene), aryl (arylene), or aralkyl (aralkylene) groups.

Other cationic surfactants effective in any glyphosate composition or formulation are diamines or diammonium salts having the formulas:

$$R_1$$
  $(R_2-O)_m$   $N$   $R_3$   $N$   $(R_2-O)_n$   $R_4$   $R_6$   $R_5$   $(16)$ 

15 or

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$$R_1$$
  $(R_2-O)_m$   $N$   $R_3$   $N$   $(R_2-O)_m$   $R_4$   $(R_4$   $R_5$ 

(17)

wherein  $R^1$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are independently hydrogen or hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms,  $R^2$  in each of the m ( $R^2O$ ) and n ( $R^2O$ ) groups and  $R^9$  are independently  $C_2$ - $C_4$  alkylene,  $R^3$  is hydrocarbylene or substituted hydrocarbylene having from about 2 to about 6 carbon atoms or -( $R^2O$ )<sub>p</sub> $R_9$ -, m and n are individually an average number from 0 to about 50, and p is an average number from 0 to about 60. In this context, preferred  $R^1$ ,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  hydrocarbyl (hydrocarbylene) groups are linear or branched alkyl (alkylene), linear or branched alkenyl (alkenylene), linear or branched alkynyl (alkynylene), aryl (arylene), or aralkyl (aralkylene) groups. In one embodiment of formula (DA),  $R^3$  is hydrocarbylene having from about 2 to about 6 carbon atoms, and the remaining groups are as defined above.

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Preferred nonionic surfactants for such glyphosate concentrates include alkoxylated alcohols having the formula:

$$R^{1}O-(R^{2}O)_{x}R^{3}$$

(18)

wherein R1 is hydrocarbyl or substituted hydrocarbyl having from 1 to about 30 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene, R<sup>3</sup> is hydrogen, or a linear or branched alkyl group having from 1 to about 4 carbon atoms, and x is an average number from 1 to about 60. In this context, preferred R1 hydrocarbyl groups are linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl groups. Preferably, R1 is a linear or branched alkyl or linear or branched alkenyl group having from about 8 to about 30 carbon atoms. R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently C<sub>2</sub>-C<sub>4</sub> alkylene, R<sup>3</sup> is hydrogen, methyl or ethyl, and x is an average number from about 5 to about 50. More preferably, R<sup>1</sup> is a linear or branched alkyl group having from about 8 to about 25 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, and x is an average number from about 8 to about 40. Even more preferably, R1 is a linear or branched alkyl group having from about 12 to about 22 carbon atoms, R2 in each of the x (R2O) groups is independently ethylene or propylene, R3 is hydrogen or methyl, and x is an average number from about 8 to about 30. Preferred commercially available alkoxylated alcohols include Procol™ LA-15 (from Protameen), Brij™ 35, Brij™ 76, Brij™ 78, Brij™ 97 and Brij™ 98 (from Sigma Chemical Co.), Neodol™ 25-12 (from Shell), Hexotol™ CA-10, Hexotol™ CA-20, Hexotol™ CS-9, Hexotol™ CS-15, Hexotol™ CS-20, Hexotol™ CS-25, Hexotol™ CS-30, and Plurafac™ A38 (from BASF), ST-8303 (from Cognis), and Arosurf™ 66 E20 (from Witco/Crompton).

Other nonionic surfactants for use in such glyphosate compositions or formulations include alkoxylated dialkylphenols having the formula:

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wherein R<sup>1</sup> and R<sup>4</sup> are independently hydrogen, or a linear or branched alkyl group having from 1 to about 30 carbon atoms and at least one of R1 and R4 is an alkyl group, R2 in each of the x (R2O) groups is independently C2-C4 alkylene, R3 is hydrogen, or a linear or branched alkyl group having from 1 to about 4 carbon atoms, and x is an average number from 1 to about 60. Preferably, R<sup>1</sup> and R<sup>4</sup> are independently linear or branched alkyl groups having from 8 to about 30 carbon atoms, R2 in each of the x (R2O) groups is independently C2-C4 alkylene, R3 is hydrogen, methyl or ethyl, and x is an average number from about 5 to about 50. More preferably, R<sup>1</sup> and R<sup>4</sup> are independently linear or branched alkyl groups having from about 8 to about 22 carbon atoms, R2 in each of the x (R2O) groups is independently ethylene or propylene, R3 is hydrogen or methyl, and x is an average number from about 8 to about 40. Even more preferably, R1 and R4 are independently linear or branched alkyl groups having from about 8 to about 16 carbon atoms, R<sup>2</sup> in each of the x (R<sup>2</sup>O) groups is independently ethylene or propylene, R<sup>3</sup> is hydrogen or methyl, and x is an average number from about 10 to about 30. Preferred commercially available alkoxylated dialkylphenols include ethoxylated dinonyl phenols such as Surfonic™ DNP 100, Surfonic™ DNP 140, and Surfonic™ DNP 240 (from Huntsman).

Preferred anionic surfactants effective in forming glyphosate compositions or formulations, in at least some embodiments, may include saturated carboxylic acids such as butyric, caproic, caprylic, capric, lauric, palmitic, myristic or stearic acid, and unsaturated carboxylic acids such as palmitoleic, oleic, linoleic or linolenic acid. Preferred carboxylic acids, in at least some embodiments, may include palmitic, oleic or stearic acid. Other preferred anionic surfactants, in at least some embodiments, may include alkyl sulfates such as sodium lauryl sulfate, and alkyl alkoxylated phosphates having the formulae:

$$R^{1}$$
— $O$ — $(R^{2}O)_{m}$ — $O$ 
 $R^{3}$ — $O$ — $(R^{2}O)_{n}$ 
 $H^{+}$ 

(20)

wherein  $R^1$  and  $R^3$  are independently a linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl group having from about 4 to about 30 carbon atoms;  $R^2$  in each of the m ( $R^2$ O) and the n ( $R^2$ O) groups is independently  $C_2$ - $C_4$  alkylene; and m and n are independently from 1 to about 30; or

$$R^{1}$$
— $O$ — $(R^{2}O)_{m}$ 
 $O$ 
 $H^{+}$ 

5 (21)

wherein  $R^1$  is a linear or branched alkyl, linear or branched alkenyl, linear or branched alkynyl, aryl, or aralkyl group having from about 8 to about 30 carbon atoms;  $R^2$  in each of the m ( $R^2$ O) groups is independently  $C_2$ - $C_4$  alkylene; and m is from 1 to about 30. Representative alkyl alkoxylated phosphates include oleth-10 phosphate, oleth-20 phosphate and oleth-25 phosphate. Other representative alkyl alkoxylated phosphates include those wherein, in (21),  $R^1$  has about 10 to about 15 carbon atoms,  $R^2$  is ethylene or propylene, and m is from about 1 to about 10, from about 2 to about 8, or about 4 to about 6.

Other exemplary surfactants that may be used in accordance with the present invention include the following species:

(22)

and

$$C_{16}^{\Gamma}H_{33}^{\Gamma}(OCH_{2}CH_{2})_{20}$$
  $\stackrel{+}{N}$   $\stackrel{-}{-}(CH_{2})_{3}$   $\stackrel{+}{-}$   $\stackrel{-}{-}(CH_{2}CH_{2}O)_{20}C_{16}H_{33}$   $\stackrel{+}{-}$   $CH_{3}$   $CH_{3}$   $CH_{3}$   $CH_{3}$ 

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In at least some embodiments of one or more of the aqueous or dry concentrates, or alternatively the ready-to-use composition, described herein, the weight ratio of glyphosate (a.e. basis) to surfactant may range from about 1:10 to 10:1 or more (e.g., from about 1:8 to 8:1, from about 1:6 to about 6:1, from about 1:4 to about 4:1, from about 1:3 to about 3:1, or from about 1:2 to about 2:1). Alternatively, this ratio may range from about 1:1 to about 10:1 (e.g., from about 1:1 to about 10:1, from about 2:1 to about 8:1, or from about 3:1 to about 6:1), from about 1:1 to about 15:1, from about 1:1 to about 20:1, or more. Accordingly, exemplary ratios include about 1:10, about 1:9.5, about 1:9, about 1:8.5, about 1:8.

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about 1:7.5, about 1:7, about 1:6.5, about 1:6, about 1:5.5, about 1:5, about 1:4.5, about 1:4, about 1:3.5, about 1:3, about 12.5, about 1:2, about 1:1.5, about 1:1, about 1.5:1, about 2:1, about 2.5:1, about 3:1, about 3.5:1, about 4:1, about 4.5:1, about 5:1, about 5:5:1, about 6:1, about 6.5:1, about 7:1, about 7:5:1, about 8:1, about 8.5:1, about 9:1, about 9:5:1, about 10:1, about 11:1, about 12:1, about 13:1, about 14:1, about 15:1, about 16:1, about 17:1, about 18:1, about 19:1, about 20:1 or more.

Alternatively, in these or other embodiments (e.g, a ready-to-use composition), the weight ratio of glyphosate (a.e. basis) to surfactant may range from about 10:1 to about 1:5 (e.g., from about 8:1 to about 1:4, from about 6:1 to about 1:3, from about 4:1 to about 1:2, or from about 2:1 to about 1:1).

Additionally, in these or other embodiments, the surfactant concentration may be at least about 1 gram per liter (e.g., at least about 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 200, 250, 300, 350, 400, 450, 500 grams per liter or more), ranging for example from about 1 to about 500 grams per liter, from about 5 to about 250 grams per liter, 10 to about 100 grams per liter, from about 20 to about 80 grams per liter, or from about 40 to about 60 grams per liter. Alternatively, the surfactant concentration may range from about 1 to 283 grams per liter (e.g., ranging for example from about 1 to about 275 grams per liter, from about 5 to about 250 grams per liter, from about 10 to about 100 grams per liter, from about 20 to about 80 grams per liter, or from about 40 to about 60 grams per liter).

In some embodiments (e.g., a ready-to-use composition), the surfactant concentration may not be greater than 3.9 grams per liter (e.g., not greater than 3.8, 3.6, 3.4, 3.2, 3, 2.8, 2.6, 2.4, 2.2, 2, 1.8, 1.6, 1.4, 1.2, 1 or less), when the weight ratio (a.e. to a.e.) of glyphosate to pyridine analog (triclopyr, for example) is at least 3:1. In these or other embodiments, the surfactant concentration may not be greater than 6.6 grams per liter (e.g., not greater than 6.4, 6.2, 6, 5.8, 5.6, 5.4, 5.2, 5, 4.8, 4.6, 4.4, 4.2, 4, 3.8, etc.), when the weight ratio (a.e. to a.e.) of glyphosate to pyridine analog (triclopyr, for example) is at least 5:1. In these or still other embodiments, the surfactant concentration may not be greater than 9.3 grams per liter (e.g., not greater than 9.2, 9. 8.8, 8.6, 8.4, 8.2, 8, 7.8, 7.6, 7.4, 7.2, 7, 6.8, 6.6, 6.4, etc.), when the weight ratio (a.e. to a.e.) of glyphosate to pyridine analog (triclopyr, for example) is at least 7:1.

### III. Properties

Among the various properties of the compositions of the present invention is to be noted that these compositions typically have a cloud point of at least about

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50°C, or even about 60°C. Additionally, the aqueous concentrate and/or the ready-to-use composition of the present invention typically has a composition such that triclopyr (or more generally the pyridine analog) will not crystallize or precipitate when the bulk solution freezes or solidifies, and then thaws; stated another way, the herbicide compositions or formulations of the present invention have a composition wherein the pyridine analog, such as triclopyr, will not precipitate upon being cooled to a temperature of about 0°C, or even about -10°C.

### IV. Optional Additives

As further discussed herein, other additives, adjuvants, or ingredients may be introduced into the compositions or formulations of the present invention to improve certain properties thereof (e.g., solubility of the pyridine analog). Although the compositions or formulations of the present invention generally show good overall stability and viscosity properties without the addition of any further additives, the addition of a solubilizer (also commonly referred to as a cloud point enhancer or stabilizer) may significantly improve the properties of the compositions or formulations of the present invention. Suitable solubilizers for use with the novel compositions or formulations of the present invention include, for example, cocoamine (Armeen C), dimethylcocoamine (Arquad DMCD), cocoammonium chloride (Arquad C), PEG 2 cocoamine (Ethomeen C12), a cocodiamine 3EO (Ethoduomeen CD/13), PEG 5 tallowamine (Ethomeen T15), and PEG 5 cocoamine (Ethomeen C15), all of which are manufactured by Akzo Nobel (California).

Additionally, it has been found that the addition of a C<sub>4</sub> to C<sub>16</sub> alkyl or aryl amine compound, or the corresponding quaternary ammonium compound, greatly enhances the compatibility of certain glyphosate salts (e.g., potassium or isopropylamine) with surfactants that otherwise exhibit low or marginal compatibility at a given glyphosate loading. Suitable alkyl or aryl amine compounds may also contain 0 to about 5 EO groups. Preferred alkylamine compounds include C<sub>6</sub> to C<sub>12</sub> alkylamines having 0 to 2 EO groups. Similarly, etheramine compounds having 4 to 12 carbons and 0 to about 5 EO groups, as well as the corresponding quaternary ammonium compounds, also enhance the compatibility of such compositions or formulations. In one embodiment, the compounds which enhance the compatibility of such surfactants include amines or quaternary ammonium salts having the formula:

$$R^1 \longrightarrow N \left( \begin{array}{c} R^2 \\ R^3 \end{array} \right)$$
 (24)

or

$$\begin{array}{ccc}
R^2 & A^{-} \\
 & \\
R^{1} & N^{+} & R^{3} \\
 & & \\
R^{4}
\end{array}$$

(25)

or

$$R^{1}O - (R^{6}O)_{\overline{n}} - R^{5} - N$$

5 (26)

or

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$$R^{1}O = (R^{6}O)_{n} - R^{5} - N^{\pm}R^{4}$$
 $R^{3}$ 
 $R^{3}$ 
(27)

wherein  $R^1$  is linear or branched alkyl or aryl having from about 4 to about 16 carbon atoms,  $R^2$  is hydrogen, methyl, ethyl, or -( $CH_2CH_2O)_xH$ ,  $R^3$  is hydrogen, methyl, ethyl, or -( $CH_2CH_2O)_yH$  wherein the sum of x and y is not more than about 5;  $R^4$  is hydrogen or methyl;  $R^6$  in each of the n ( $R^6O$ ) groups is independently  $C_2$ - $C_4$  alkylene;  $R^5$  is hydrocarbylene or substituted hydrocarbylene having from 2 to about 6 carbon atoms; and A- is an agriculturally acceptable anion.

Optionally, one or more of the compositions of the present invention may further comprise one or more additional pesticides, such as for example, water-soluble herbicidal active ingredients, including without restriction water-soluble forms of acifluorfen, asulam, benazolin, bentazon, bialaphos, bispyribac, bromacil, bromoxynil, carfentrazone, chloramben, 2,4-D, 2,4-DB, dalapon, dicamba, dichlorprop, diclofop, difenzoquat, diquat, endothall, fenac, fenoxaprop, flamprop, fluazifop, fluoroglycofen, fomesafen, fosamine, glufosinate, haloxyfop, imazameth,

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imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, ioxynil, MCPA, MCPB, mecoprop, methylarsonic acid, naptalam, nonanoic acid, paraquat, sulfamic acid, 2,3,6-TBA, TCA, acetochlor, aclonifen, alachlor, ametryn, amidosulfuron, anilofos, atrazine, azafenidin, azimsulfuron, benfluralin, benfuresate, bensulfuron-methyl, bensulide, benzofenap, bifenox, bromobutide, bromofenoxim, butachlor, butamifos, butralin, butroxydim, butylate, cafenstrole, carbetamide, carfentrazone-ethyl, chlomethoxyfen, chlorbromuron, chloridazon, chlorimuron-ethyl, chlornitrofen, chlorotoluron, chlorpropham, chlorsulfuron, chlorthal-dimethyl, chlorthiamid, cinmethylin, cinosulfuron, clethodim, clodinafop-propargyl, clomazone, clomeprop, cloransulam-methyl, cyanazine, cycloate, cyclosulfamuron, cycloxydim, cyhalofop-butyl, daimuron, desmedipham, desmetryn, dichlobenil, diclofop-methyl, diflufenican, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dinitramine, dinoterb, diphenamid, diuron, EPTC, esprocarb, ethalfluralin, ethametsulfuron-methyl, ethofumesate, ethoxysulfuron, etobenzanid, fenoxapropethyl, fenuron, flamprop-methyl, flazasulfuron, fluazifop-butyl, fluchloralin, flumetsulam, flumiclorac-pentyl, flumioxazin, fluometuron, fluorochloridone, fluoroglycofen-ethyl, flupoxam, flurenol, fluridone, flurtamone, fluthiacet-methyl, fomesafen, halosulfuron, haloxyfop-methyl, hexazinone, imazosulfuron, indanofan, isoproturon, isouron, isoxaben, isoxaflutole, isoxapyrifop, lactofen, lenacil, linuron, mefenacet, metamitron, metazachlor, methabenzthiazuron, methyldymron, metobenzuron, metobromuron, metolachlor, metosulam, metoxuron, metribuzin, metsulfuron, molinate, monolinuron, naproanilide, napropamide, naptalam, neburon, nicosulfuron, norflurazon, orbencarb, oryzalin, oxadiargyl, oxadiazon, oxasulfuron, oxyfluorfen, pebulate, pendimethalin, pentanochlor, pentoxazone, phenmedipham, piperophos, pretilachlor, primisulfuron, prodiamine, prometon, prometryn, propachlor, propanil, propaguizafop, propazine, propham, propisochlor, propyzamide, prosulfocarb, prosulfuron, pyraflufen-ethyl, pyrazolynate, pyrazosulfuron-ethyl, pyrazoxyfen, pyributicarb, pyridate, pyriminobac-methyl, quinclorac, quinmerac, quizalofop-ethyl, rimsulfuron, sethoxydim, siduron, simazine, simetryn, sulcotrione, sulfentrazone, sulfometuron, sulfosulfuron, tebutam. tebuthiuron, terbacil, terbumeton, terbuthylazine, terbutryn, thenylchlor, thifensulfuron, thiobencarb, tiocarbazil, tralkoxydim, triallate, triasulfuron, tribenuron, trietazine, trifluralin, triflusulfuron and vernolate.

Another ingredient that can optionally be added to the glyphosate herbicidal compositions or formulations of the present invention to further improve the herbicidal effectiveness and related herbicidal properties is a di-carboxylic acid or salt of a di-carboxylic acid. Suitable di-carboxylic acids that may be added to the herbicidal compositions or formulations comprising glyphosate or a salt or ester

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thereof and a surfactant as described herein include, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, maleic acid, adipic acid, and fumaric acid, and combinations or mixtures thereof, with oxalic acid being preferred. Also, in addition to, or in place of the di-carboxylic acid, salts of the aforementioned di-carboxylic acids may be incorporated into the herbicidal formulations of the present invention to improve herbicidal performance. Suitable salts include, for example, alkali metal salts such as potassium salts, alkanolamine salts and lower alkylamine salts. Preferred salts include potassium oxalate, dipotassium oxalate, sodium oxalate, disodium oxalate, diammonium oxalate, diethanolamine oxalate, dimethylamine oxalate, alkanolamine salts of oxalic acid, and lower alkylamine salts of oxalic acid.

Formulations containing a di-carboxylic acid such as oxalic acid or a di-carboxylic acid salt such as potassium oxalate, typically contain a sufficient amount of di-carboxylic acid/di-carboxylic acid salt to enhance the resulting efficacy of the herbicidal formulation. The weight ratio of total surfactant to carboxylic acid/carboxylic acid salt may be, for example, from about 1:1 to about 50:1, about 5:1 to about 40:1, or even about 5:1 to about 20:1. This ratio of total surfactant to carboxylic acid/carboxylic acid salt may significantly enhance the herbicidal performance of the resulting herbicidal formulation.

The di-carboxylic acid or salt thereof which can be added to herbicidal formulations of the present invention to improve efficacy are suitable for use with glyphosate, or salts thereof. Suitable glyphosate salts include those listed above, such as for example the isopropylamine salt, the potassium salt, and the trimethylammonium salt.

In this regard it is to be noted that U.S. Patent Application Serial No. 09/988,353 (entitled Pesticide Compositions Containing Oxalic Acid and published on September 5, 2002 under Publication No. US-2002-0123430-A1) is incorporated herein by reference, as well as U.S. Patent Application Serial No. 10/653,332 (entitled Process for the Preparation of a Dry Pesticidal Composition Containing a Dicarboxylate Component and filed on September 2, 2003) and U.S. Patent Application Serial No. 10/653,047 (entitled Pesticidal Compositions Containing Dicarboxylic Acids and filed on August 29, 2003).

Yet another ingredient that can optionally be added to one or more of the compositions of the present invention is a fatty acid (e.g., a C<sub>8</sub> to C<sub>12</sub> fatty acid). For example, in at least one embodiment the present invention is directed to a composition (e.g., a solid or liquid concentrate, or alternatively a ready-to-use composition) comprising glyphosate (or a derivative thereof), triclopyr or other

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pyridine analog (or a derivative thereof), a pelargonic acid (or nonanoic acid) or derivative thereof, and a surfactant, such as a linear alcohol ethoxylate.

Excipient ingredients other than the above-defined surfactant component can optionally be present in a composition of the invention, so long as the cloud point and non-crystallization properties of the composition remain in accordance with the invention. Such additional excipient ingredients may include conventional formulation additives such as dyes, thickeners, crystallization inhibitors, antifreeze agents (e.g., glycols, such a ethylene glycol), foam moderating agents (e.g., Antifoam<sup>TM</sup> or Y-14088 Antifoam<sup>TM</sup>, both available from Crompton Corporation), antidrift agents, compatibilizing agents, antioxidants (e.g., ascorbic acid and sodium sulfite, in order for example to prevent the formation of a nitrosamine), other cosolvents (e.g., N-methylpyrrolidone, DMSO, DMF, propylene carbonate, or ethylene glycol), or some other agent added to lessen or overcome antagonism associated with hard water (e.g., ammonium sulfate, EDTA or a polymeric water conditioner, such as a polyacrylic acid), etc.

#### V. Formulations

The herbicidal compositions of the invention can be prepared on site by the end-user shortly before application to the foliage of the vegetation to be killed or controlled by mixing in an aqueous solution (i) glyphosate or a herbicidal derivative thereof, (ii) a pyridine analog, such as triclopyr, or a derivative thereof, and (iii) a suitable surfactant. Such compositions are typically referred to as "tank-mix" compositions. Typically, herbicidal compositions of the present invention that are ready to be applied directly to foliage can be made with a glyphosate concentration as described elsewhere herein. Additionally, such herbicidal compositions can be made with a triclopyr, or some other pyridine analog, at a concentration also as described elsewhere herein. However, it is to be noted that one skilled in the art will recognize that various factors influence the application rate of glyphosate and, for example, triclopyr (or another pyridine analog), required for a desired result. As a result, the concentration of such compositions may be other than as described herein without departing from the scope of the present invention.

Alternatively, the herbicidal compositions of the invention may be provided to the end-user already formulated, either at the desired dilution for application (i.e., "ready-to-use" compositions) or requiring dilution, dispersion, or dissolution in water by the end-user (i.e., "concentrate" compositions, wherein the glyphosate concentration is at least about 50 grams (a.e.) per liter). Such preformulated concentrates can be liquids or particulate solids.

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With respect to the particulate solids, or dry formulations, of the present invention, it is to be noted that these may be in the form of powders, pellets, tablets or granules. These dry formulations are typically dispersed or dissolved into water prior to use. Preferably, there are no substantially water insoluble constituents present at substantial levels in the such formulations such that the formulations are substantially water soluble. Dry water-soluble or water-dispersable formulations of the present invention typically comprise the same ratios of glyphosate to triclopyr (G:T), or more generally the same ratios of glyphosate to pyridine analog, and glyphosate to surfactant (G:S), as described elsewhere herein. With respect to the load of the composition ingredients (i.e., glyphosate, triclopyr, or other pyridine analog, and surfactant), as well as the particular ingredients themselves, it is to be noted that the selection of these for a given application may be determined in view of commercial consideration, and using means, known in the art.

In dry formulations of the present invention, the glyphosate itself may provide the support for other formulation constituents, or there may be additional inert ingredients which provide such support. One example of an inert support ingredient that may be used in accordance with the present invention is ammonium sulfate. It will be recognized by one skilled in the art that as used herein, the term "dry" does not imply that dry formulations of the present invention are 100% free of water. Typically, dry formulations of the present invention comprise from about 0.5% to about 5% (by weight) water. It is preferred that the dry formulations of the present invention contain less than about 1% (by weight) water. Additionally, it is preferred for at least some embodiments that the particulate solid exhibits a dissolution rate of not more than about 5 minutes, about 4 minutes, about 3 minutes, about 2 minutes, or even about 1 minute.

Dry, water soluble or water dispersable formulations in accordance with the present invention can be produced by any process known in the art, including spray drying, fluid-bed agglomeration, pan granulation, or extrusion. In dry formulations, glyphosate may be present as a salt, or as an acid. Formulations containing glyphosate acid may optionally contain an acid acceptor such as an ammonium or alkali metal carbonate or bicarbonate, ammonium dihydrogen phosphate or the like so that upon dissolution or dispersion in water by the user a water soluble salt of glyphosate is produced.

Also embraced by the present invention are liquid concentrate formulations having an aqueous phase wherein glyphosate is present predominantly in the form of a salt, and a non-aqueous phase optionally containing a second herbicidal active ingredient that is relatively water-insoluble. Such formulations illustratively include emulsions (including macro- and microemulsions, water-in-oil, oil-in-water and water-

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in-oil-in-water types), suspensions and suspoemulsions. The non-aqueous phase can optionally comprise a microencapsulated component, for example a microencapsulated herbicide. In formulations of the invention having a non-aqueous phase, the concentration of glyphosate a.e. in the composition as a whole is nonetheless within the ranges recited herein for aqueous concentrate formulations.

Illustrative water-insoluble herbicides that can be used in such formulations include acetochlor, aclonifen, alachlor, ametryn, amidosulfuron, anilofos, atrazine, azafenidin, azimsulfuron, benfluralin, benfuresate, bensulfuron-methyl, bensulide, benzofenap, bifenox, bromobutide, bromofenoxim, butachlor, butamifos, butralin, butroxydim, butylate, cafenstrole, carbetamide, carfentrazone-ethyl, chlomethoxyfen, chlorbromuron, chloridazon, chlorimuron-ethyl, chlornitrofen, chlorotoluron, chlorpropham, chlorsulfuron, chlorthal-dimethyl, chlorthiamid, cinmethylin, cinosulfuron, clethodim, clodinafop-propargyl, clomazone, clomeprop, cloransulammethyl, cyanazine, cycloate, cyclosulfamuron, cycloxydim, cyhalofop-butyl, daimuron, desmedipham, desmetryn, dichlobenil, diclofop-methyl, diflufenican, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dinitramine, dinoterb, diphenamid, diuron, EPTC, esprocarb, ethalfluralin, ethametsulfuronmethyl, ethofumesate, ethoxysulfuron, etobenzanid, fenoxaprop-ethyl, fenuron, flamprop-methyl, flazasulfuron, fluazifop-butyl, fluchloralin, flumetsulam, flumicloracpentyl, flumioxazin, fluometuron, fluorochloridone, fluoroglycofen-ethyl, flupoxam, flurenol, fluridone, flurtamone, fluthiacet-methyl, fomesafen, halosulfuron, haloxyfopmethyl, hexazinone, imazosulfuron, indanofan, isoproturon, isouron, isoxaben, isoxaflutole, isoxapyrifop, lactofen, lenacil, linuron, mefenacet, metamitron, metazachlor, methabenzthiazuron, methyldymron, metobenzuron, metobromuron, metolachlor, metosulam, metoxuron, metribuzin, metsulfuron, molinate, monolinuron, naproanilide, napropamide, naptalam, neburon, nicosulfuron, norflurazon, orbencarb, oryzalin, oxadiargyl, oxadiazon, oxasulfuron, oxyfluorfen, pebulate, pendimethalin, pentanochlor, pentoxazone, phenmedipham, piperophos, pretilachlor, primisulfuron, prodiamine, prometon, prometryn, propachlor, propanil, propaguizafop, propazine, propham, propisochlor, propyzamide, prosulfocarb, prosulfuron, pyraflufen-ethyl, pyrazolynate, pyrazosulfuron-ethyl, pyrazoxyfen, pyributicarb, pyridate, pyriminobac-methyl, quinclorac, quinmerac, quizalofop-ethyl, rimsulfuron, sethoxydim, siduron, simazine, simetryn, sulcotrione, sulfentrazone, sulfometuron, sulfosulfuron, tebutam, tebuthiuron, terbacil, terbumeton, terbuthylazine, terbutryn, thenylchlor, thifensulfuron, thiobencarb, tiocarbazil, tralkoxydim, triallate, triasulfuron, tribenuron, trietazine, trifluralin, triflusulfuron and vernolate.

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It is to be noted that the herbicidal spray compositions of the present invention are applied as aqueous solutions or dispersions, whether they result from the further dilution of the liquid concentrate or the addition of water to the particulate solid concentrate. However, the term "aqueous," as used herein, is not intended to exclude the presence of some small amount of nonaqueous solvent, so long as the predominant solvent present, other than for example the glycol or glycol ester component of the surfactant composition, is water.

### VI. Application

Generally speaking, the present invention is additionally directed to a method of for killing or controlling weeds or unwanted vegetation which comprises the steps of diluting a liquid concentrate in a convenient amount of water to form a tank mix and applying a herbicidally effective amount of the tank mix to the foliage of the weeds or unwanted vegetation. Similarly included in the invention is the method of killing or controlling weeds or unwanted vegetation comprising the steps of diluting a solid particulate concentrate in a convenient amount of water to form a tank mix and applying a herbicidally effective amount of the tank mix to the foliage of the weeds or unwanted vegetation.

The herbicidal composition of the present invention is applied to plants at a rate sufficient to give the desired biological effects: control of plant growth and early visual symptoms of treatment. The amount of glyphosate and triclopyr, or other pyridine analog, applied to plants in combination generally provides a herbicidallyeffective amount of the herbicides. The amount of glyphosate and triclopyr, or other pyridine analogy, applied to plants further is sufficient to provide early visual symptoms of plant treatment without significantly reducing the desired biological effect of the glyphosate. These application rates are usually expressed as amount of glyphosate per unit area treated, e.g. grams per hectare (g/ha). What constitutes a "desired effect" varies according to the standards and practice of those who investigate, develop, market and use compositions. Typically, the amount of the composition applied per unit area to give 85% control of a plant species as measured by growth reduction or mortality is often used to define a commercially effective rate. Early visual symptoms of treatment typically appear no later than about 4 days after treatment, preferably no later than about 3 days after treatment, more preferably no later than about 2 days after treatment, and still more preferably no later than about 1 day after treatment.

The selection of application rates that are herbicidally effective for a composition of the invention is within the skill of the ordinary agricultural scientist.

Those of skill in the art will likewise recognize that individual plant conditions, weather and growing conditions, as well as the specific active ingredients and their weight ratio in the composition, will influence the degree of herbicidal effectiveness achieved in practicing this invention. With respect to the use of glyphosate compositions, much information is known about appropriate application rates. Over two decades of glyphosate use and published studies relating to such use have provided abundant information from which a weed control practitioner can select glyphosate application rates that are herbicidally effective on particular species at particular growth stages in particular environmental conditions.

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The herbicidal spray compositions included in the present invention can be applied to the foliage of the plants to be treated through any of the appropriate methods that are well known to those having skill in the art. However, in one embodiment, the herbicidal composition is applied using means other than a helicopter; stated another way, in at least some embodiments the present invention is directed to methods wherein the herbicidal composition is applied using non-aerial means (i.e., ground application techniques. such as a hand sprayer, rope-wick, etc.) or using a fixed-wing aircraft.

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Particularly important annual dicotyledonous plant species for control of which a composition of the invention can be used are exemplified without limitation by velvetleaf (*Abutilon theophrasti*), pigweed (*Amaranthus spp.*), buttonweed (*Borreria spp.*), oilseed rape, canola, indian mustard, etc. (*Brassica spp.*), commelina (*Commelina spp.*), filaree (*Erodium spp.*), sunflower (*Helianthus spp.*), morningglory (*Ipomoea spp.*), kochia (*Kochia scoparia*), mallow (*Malva spp.*), wild buckwheat, smartweed, etc. (*Polygonum spp.*), purslane (*Portulaca spp.*), russian thistle (*Salsola spp.*), sida (*Sida spp.*), wild mustard (*Sinapis arvensis*) and cocklebur (*Xanthium spp.*).

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Particularly important annual monocotyledonous plant species for control of which a composition of the invention can be used are exemplified without limitation by wild oat (*Avena fatua*), carpetgrass (*Axonopus spp.*), downy brome (*Bromus tectorum*), crabgrass (*Digitaria spp.*), barnyardgrass (*Echinochloa crus-galli*), goosegrass (*Eleusine indica*), annual ryegrass (*Lolium multiflorum*), rice (*Oryza sativa*), ottochloa (*Ottochloa nodosa*), bahiagrass (*Paspalum notatum*), canarygrass (*Phalaris spp.*), foxtail (*Setaria spp.*), wheat (*Triticum aestivum*) and corn (*Zea mays*):

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Particularly important perennial dicotyledonous plant species for control of which a composition of the invention can be used are exemplified without limitation by mugwort (*Artemisia spp.*), milkweed (*Asclepias spp.*), canada thistle (*Cirsium arvense*), field bindweed (*Convolvulus arvensis*) and kudzu (*Pueraria spp.*).

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Particularly important perennial monocotyledonous plant species for control of which a composition of the invention can be used are exemplified without limitation by brachiaria (*Brachiaria spp.*), bermudagrass (*Cynodon dactylon*), yellow nutsedge (*Cyperus esculentus*), purple nutsedge (*C. rotundus*), quackgrass (*Elymus repens*), lalang (*Imperata cylindrica*), perennial ryegrass (*Lolium perenne*), guineagrass (*Panicum maximum*), dallisgrass (*Paspalum dilatatum*), reed (*Phragmites spp.*), johnsongrass (*Sorghum halepense*) and cattail (*Typha spp.*).

Other particularly important perennial plant species for control of which a composition of the invention can be used are exemplified without limitation by horsetail (*Equisetum spp.*), bracken (*Pteridium aquilinum*), blackberry (*Rubus spp.*) and gorse (*Ulex europaeus*).

If desired, the user can mix one or more adjuvants with a composition of the invention and the water of dilution when preparing the application composition. Such adjuvants can include additional surfactant and/or an inorganic salt such as ammonium sulfate with the aim of further enhancing herbicidal efficacy. However, under most conditions a herbicidal method of use of the present invention gives acceptable efficacy in the absence of such adjuvants.

In a particular contemplated method of use of a composition of the invention, the composition, following dilution in water, is applied to foliage of crop plants genetically transformed or selected to tolerate glyphosate, and simultaneously to foliage of weeds or undesired plants growing in close proximity to such crop plants. This method of use results in control of the weeds or undesired plants while leaving the crop plants substantially unharmed. Crop plants genetically transformed or selected to tolerate glyphosate include those whose seeds are sold by Monsanto Company or under license from Monsanto Company bearing the Roundup Ready® trademark. These include, without restriction, varieties of cotton, soybean, canola, sugar beet, wheat and corn.

Plant treatment compositions can be prepared simply by diluting a concentrate composition of the invention in water. Application of plant treatment compositions to foliage is preferably accomplished by spraying, using any conventional means for spraying liquids, such as spray nozzles, atomizers or the like. Compositions of the invention can be used in precision farming techniques, in which apparatus is employed to vary the amount of pesticide applied to different parts of a field, depending on variables such as the particular plant species present, soil composition, etc. In one embodiment of such techniques, a global positioning system operated with the spraying apparatus can be used to apply the desired amount of the composition to different parts of a field.

#### VII. Definitions

The terms "hydrocarbon" and "hydrocarbyl" as used herein describe organic compounds or radicals consisting exclusively of the elements carbon and hydrogen. These moieties include alkyl, alkenyl, alkynyl, and aryl moieties. These moieties also include alkyl, alkenyl, alkynyl, and aryl moieties substituted with other aliphatic or cyclic hydrocarbon groups, such as alkaryl, alkenaryl and alkynaryl. Unless otherwise indicated, these moieties preferably comprise 1 to 30 carbon atoms.

The term "hydrocarbylene" as used herein describes radicals joined at two ends thereof to other radicals in an organic compound, and which consist exclusively of the elements carbon and hydrogen. These moieties include alkylene, alkenylene, alkynylene, and arylene moieties. These moieties also include alkyl, alkenyl, alkynyl, and aryl moieties substituted with other aliphatic or cyclic hydrocarbon groups, such as alkaryl, alkenaryl and alkynaryl. Unless otherwise indicated, these moieties preferably comprise 1 to 30 carbon atoms.

The "substituted hydrocarbyl" moieties described herein are hydrocarbyl moieties which are substituted with at least one atom other than carbon, including moieties in which a carbon chain atom is substituted with a hetero atom such as nitrogen, oxygen, silicon, phosphorous, boron, sulfur, or a halogen atom. These substituents include halogen, heterocyclo, alkoxy, alkenoxy, alkynoxy, aryloxy, hydroxy, protected hydroxy, ketal, acyl, acyloxy, nitro, amino, amido, cyano, thiol, acetal, sulfoxide, ester, thioester, ether, thioether, hydroxyalkyl, urea, guanidine, amidine, phosphate, amine oxide, and quaternary ammonium salt.

The "substituted hydrocarbylene" moieties described herein are hydrocarbylene moieties which are substituted with at least one atom other than carbon, including moieties in which a carbon chain atom is substituted with a hetero atom such as nitrogen, oxygen, silicon, phosphorous, boron, sulfur, or a halogen atom. These substituents include halogen, heterocyclo, alkoxy, alkenoxy, alkynoxy, aryloxy, hydroxy, protected hydroxy, ketal, acyl, acyloxy, nitro, amino, amido, cyano, thiol, acetal, sulfoxide, ester, thioester, ether, thioether, hydroxyalkyl, urea, guanidine, amidine, phosphate, amine oxide, and quaternary ammonium salt.

Unless otherwise indicated, the alkyl groups described herein are preferably lower alkyl containing from one to 18 carbon atoms in the principal chain and up to 30 carbon atoms. They may be straight or branched chain or cyclic and include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, hexyl, 2-ethylhexyl, and the like.

Unless otherwise indicated, the alkenyl groups described herein are preferably lower alkenyl containing from two to 18 carbon atoms in the principal

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chain and up to 30 carbon atoms. They may be straight or branched chain or cyclic and include ethenyl, propenyl, isopropenyl, butenyl, isobutenyl, hexenyl, and the like.

Unless otherwise indicated, the alkynyl groups described herein are preferably lower alkynyl containing from two to 18 carbon atoms in the principal chain and up to 30 carbon atoms. They may be straight or branched chain and include ethynyl, propynyl, butynyl, isobutynyl, hexynyl, and the like.

The terms "aryl" as used herein alone or as part of another group denote optionally substituted homocyclic aromatic groups, preferably monocyclic or bicyclic groups containing from 6 to 12 carbons in the ring portion, such as phenyl, biphenyl, naphthyl, substituted phenyl, substituted biphenyl or substituted naphthyl. Phenyl and substituted phenyl are the more preferred aryl.

The term "aralkyl" as used herein denotes a group containing both alkyl and aryl structures such as benzyl.

As used herein, the alkyl, alkenyl, alkynyl, aryl and aralkyl groups can be substituted with at least one atom other than carbon, including moieties in which a carbon chain atom is substituted with a hetero atom such as nitrogen, oxygen, silicon, phosphorous, boron, sulfur, or a halogen atom. These substituents include hydroxy, nitro, amino, amido, nitro, cyano, sulfoxide, thiol, thioester, thioether, ester and ether, or any other substituent which can increase the compatibility of the surfactant and/or its efficacy enhancement in the glyphosate formulation without adversely affecting the storage stability of the formulation.

The terms "halogen" or "halo" as used herein alone or as part of another group refer to chlorine, bromine, fluorine, and iodine. Fluorine substituents are often preferred in surfactant compounds.

Unless otherwise indicated, the term "hydroxyalkyl" includes alkyl groups substituted with at least one hydroxy group, and includes bis(hydroxyalkyl)alkyl, tris(hydroxyalkyl)alkyl and poly(hydroxyalkyl)alkyl groups. Preferred hydroxyalkyl groups include hydroxymethyl (-CH $_2$ OH), and hydroxyethyl (-C $_2$ H $_4$ OH), bis(hydroxymethyl)methyl (-CH(CH $_2$ OH) $_2$ ), and tris(hydroxymethyl)methyl (-C(CH $_2$ OH) $_3$ ).

The term "cyclic" as used herein alone or as part of another group denotes a group having at least one closed ring, and includes alicyclic, aromatic (arene) and heterocyclic groups.

The terms "heterocyclo" or "heterocyclic" as used herein alone or as part of another group denote optionally substituted, fully saturated or unsaturated, monocyclic or bicyclic, aromatic or nonaromatic groups having at least one heteroatom in at least one ring, and preferably 5 or 6 atoms in each ring. The heterocyclo group preferably has 1 or 2 oxygen atoms, 1 or 2 sulfur atoms, and/or 1

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to 4 nitrogen atoms in the ring, and may be bonded to the remainder of the molecule through a carbon or heteroatom. Exemplary heterocyclo include heteroaromatics such as furyl, thienyl, pyridyl, oxazolyl, pyrrolyl, indolyl, quinolinyl, or isoquinolinyl and the like, and non-aromatic heterocyclics such as tetrahydrofuryl, tetrahydrothienyl, piperidinyl, pyrrolidino, etc. Exemplary substituents include one or more of the following groups: hydrocarbyl, substituted hydrocarbyl, keto, hydroxy, protected hydroxy, acyl, acyloxy, alkoxy, alkenoxy, alkynoxy, aryloxy, halogen, amido, amino, nitro, cyano, thiol, thioester, thioether, ketal, acetal, ester and ether.

The term "heteroaromatic" as used herein alone or as part of another group denote optionally substituted aromatic groups having at least one heteroatom in at least one ring, and preferably 5 or 6 atoms in each ring. The heteroaromatic group preferably has 1 or 2 oxygen atoms, 1 or 2 sulfur atoms, and/or 1 to 4 nitrogen atoms in the ring, and may be bonded to the remainder of the molecule through a carbon or heteroatom. Exemplary heteroaromatics include furyl, thienyl, pyridyl, oxazolyl, pyrrolyl, indolyl, quinolinyl, or isoquinolinyl and the like. Exemplary substituents include one or more of the following groups: hydrocarbyl, substituted hydrocarbyl, keto, hydroxy, protected hydroxy, acyl, acyloxy, alkoxy, alkenoxy, alkynoxy, aryloxy, halogen, amido, amino, nitro, cyano, thiol, thioether, thioester, ketal, acetal, ester and ether.

The term "acyl," as used herein alone or as part of another group, denotes the moiety formed by removal of the hydroxyl group from the group -COOH of an organic carboxylic acid, e.g., RC(O)-, wherein R is R¹, R¹O-, R¹R²N-, or R¹S-, R¹ is hydrocarbyl, heterosubstituted hydrocarbyl, or heterocyclo and R² is hydrogen, hydrocarbyl or substituted hydrocarbyl.

The term "acyloxy," as used herein alone or as part of another group, denotes an acyl group as described above bonded through an oxygen linkage (-O-), e.g., RC(O)O- wherein R is as defined in connection with the term "acyl."

The term "pesticide" includes chemicals and microbial agents used as active ingredients of products for control of crop and lawn pests and diseases, animal ectoparasites, and other pests in public health. The term also includes plant growth regulators, pest repellants, synergists, herbicide safeners (which reduce the phytotoxicity of herbicides to crop plants) and preservatives, the delivery of which to the target may expose dermal and especially ocular tissue to the pesticide. Such exposure can arise by drift of the pesticide from the delivery means to the person performing the application of the pesticide or being present in the vicinity of an application.

When a maximum or minimum "average number" is recited herein with reference to a structural feature such as oxyethylene units or glucoside units, it will

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be understood by those skilled in the art that the integer number of such units in individual molecules in a surfactant preparation typically varies over a range that can include integer numbers greater than the maximum or smaller than the minimum "average number". The presence in a composition of individual surfactant molecules having an integer number of such units outside the stated range in "average number" does not remove the composition from the scope of the present invention, so long as the "average number" is within the stated range and other requirements are met.

Herbicidal effectiveness is one of the biological effects that can be enhanced through this invention. "Herbicidal effectiveness," as used herein, refers to any observable measure of control of plant growth, which can include one or more of the actions of (1) killing, (2) inhibiting growth, reproduction or proliferation, and (3) removing, destroying, or otherwise diminishing the occurrence and activity of plants. The herbicidal effectiveness data set forth herein report "control" as a percentage following a standard procedure in the art which reflects a visual assessment of plant mortality and growth reduction by comparison with untreated plants, made by technicians specially trained to make and record such observations. In all cases, a single technician makes all assessments of percent control within any one experiment or trial. Such measurements are relied upon and regularly reported by Monsanto Company in the course of its herbicide business.

### **EXAMPLES**

The following Examples are provided for illustrative purposes only and are not intended to limit the scope of the present invention. The Examples will permit better understanding of the invention and perception of its advantages and certain variations of execution.

#### **SECTION 1. FORMULATIONS**

Aqueous herbicide formulations were generated from commercially available glyphosate isopropylamine, triclopyr triethylamine and various surfactants in the ratios indicated in Tables 1.1 and 1.2.

Table 1.1. Formulations:

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CODE	Glyphosate (G); g ae/L ³	Triclopyr (T); g ae/L <sup>a</sup>	G:T w:w <sup>b</sup>	Surfactant	Surf w/v % <sup>c</sup>	G:surf w:w d
RUP1	351 ae (30.6%)	9 40/2		FS1	11.9	3.0
RUP2	443 ae (37.2%)			FS1	9.81	4.5
RU1	27% Roundup			FS4	4.11	3.5
					<del></del>	
FG1	46.3% ae					
F2M	142	7.71	18.5:1	FS1	4.11	3.5
F1M	142	3.85	18.5:0.5	FS1	4.11	3.5
F1C	142	3.85	18.5:0.5	FS4	5.4	3.6
F2C	142	7.66	18.5:1	FS4	5.3	3.6
F3M	143	15.4	18.6:2	FS1	4.11	3.5
F5M	7.38	0.72	20.5:2	FS1	0.21	3.6
F4C	151.3	24.48	18.5:3	FS4	5.7	3.6
F11M	7.38	0.36	20.5:1	FS1	0.21	3.6
F8M	142	92.5	18.5:12	FS1	4.11	3.5
F9M	142	61.7	18.5:8	FS1	4.11	3.5
F10M	142	40.9	18.5:5.3	FS1	4.11	3.5

<sup>&</sup>lt;sup>a</sup> Glyphosate and triclopyr are expressed as the acid equivalent load (g ae/L). The densities of the concentrate formulations are in the range 1.06 to 1.17 g/ml. The ready-to-use formulation has a density of approx. 1.004g/ml.

<sup>&</sup>lt;sup>b</sup> The glyphosate/triclopyr w/w ratio given in terms of the acid equivalent weights.

<sup>&</sup>lt;sup>c</sup> The surfactant load is expressed as the weight/volume %, i.e. g/100ml.

<sup>&</sup>lt;sup>d</sup> The glyphosate/surfactant w/w ratio, i.e., g ae/g surfactant per kg of formulation.

Table 1.2. Formulations.

CODE	Glyphosate (G); g/Kg (62% ai) <sup>a</sup>	Triclopyr (T); g/Kg; (44% ai) <sup>b</sup>	G:T w:w °	Surfactant	w/w; % d
F14X	290.3	25.5	18:1.13	FS3	5
F13X	290.3	51	18:2.25	FS3	5
F12X	290.3	101	18:4.50	FS3	5
F6X	290.4	60	18:2.66	FS3	5
F4X	290.4	67.6	18:3	FS3	5
F3X	290.3	45	18:2	FS3	5
F2X	290.3	22.5	18:1	FS3	5
F1X	290.3	11.3	18:0.5	FS3	5
F0X	290.3	0	18:0	FS3	5
F14M	290.3	25.5	18:1.13	FS1	5
F13M	290.3	51	18:2.25	FS1	5
F12M	290.3	101	18:4.50	FS1	5
F6M	290.4	60	18:2.66	FS1	5
F4M	290.4	67.6	18:3	FS1	5
F5M	16.1	2.3	1:0.1	FS1	5
F3M	290.3	45	18:2	FS1	5
F2M	290.3	22.5	18:1	FS1	5
F1M	290.3	11.3	18:0.5	FS1	5
FOM	290.3	0	18:0	FS1	5
F15C	290.3	152.2	18:6.76	FS4	5
F14C	290.3	25.5	18:1.13	FS4	5
F13C	290.3	51	18:2.25	FS4	5
F12C	290.3	101	18:4.50	FS4	5
F4C	290.3	67.6	18:3	FS4	5
F3C	290.3	45	18:2	FS4	5
F2C	290.3	22.5	18:1	FS4	5
F1C	290.3	11.3	18:0.5	FS4	5

F0C	290.3	0	18:0	FS4	5
F6Y	290.3	59.9	18:2.66	FS5	3.5
F3Y	290.3	45	18.2	FS5	3.5
F4Y	290.3	67.6	18:3	FS5	3.5
F7Y	290.3	90.1	18:4	FS5	3.5

<sup>&</sup>lt;sup>a</sup> Glyphosate load expressed as the weight of a standard (62% ai glyphosate) used per 1000g. The densities of the concentrate formulations are in the range 1.06 to 1.17 g/ml. The ready-to-use formulation has a density of approx. 1.004g/ml.

#### 15 KEY TO SURFACTANTS:

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- 1. FS1 surfactant composition is a mixture of tallowamines and phosphate esters, as described in U.S. Patent No. 5,703,015.
- 2. FS2 surfactant composition is a mixture of tallowamines and phosphate esters, as described in U.S. Patent No. 5,703,015.
- FS3 surfactant composition is a mixture of a tallowamine ethoxylate with other surfactants.
  - 4. FS4 is a Cocoamine 5EO.
  - 5. FS5 is a Cocoamine 5EO.

#### **SECTION 2. STABILITY TEST & RESULTS:**

### 25 Example 2.1: Stability Test

#### Materials & Methods:

Various formulations were maintained at constant temperature for a fixed period and monitored for changes in color, homogeneity and appearance after thawing. The formulations were also cycled through temperature extremes i.e., at low temperatures of -20°C and -5°C for the fixed period then raised to the higher temperatures of 20°C and 5°C respectively and changes monitored. Results for a 4-week study are tabulated below.

<sup>&</sup>lt;sup>b</sup> Triclopyr load expressed as the weight of a standard (44.3% ai triclopyr) used per 1000g. The densities of the concentrate formulations are in the range 1.06 to 1.17 g/ml. The ready-to-use formulation has a density of approx. 1.004g/ml.

<sup>&</sup>lt;sup>c</sup> The glyphosate/triclopyr w/w ratio is given in terms of the %ai/%ai.

<sup>&</sup>lt;sup>d</sup> The surfactant is expressed as the w/w% i.e., weight of surfactant standard per 100g.

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Results: Table 2.1A. Stability Results.

Temperature Stability Results (4 weeks)	-20/+20  -5/+5 °C   4.5 °C   60 °C  -10 °C   Apperance after °C   thawing to Room Temp.	-19.9 °C)[(-6.7 °C)]	Color at No No Solid, No crystals,	bottom change change crystals homogenous	Color at No No Solid, No crystals,	S	Color at No No Solid, No crystals,	bottom change change crystals homogenous	Color of No No Operate	change change change cauctals	_	X'tals No No Solid, Crystals remain on	10% change change crystals bottom (10%) (btm)	Color at No No Solid, No crystals,	bottom change change crystals homogenous	Color at No No Solid, No crystals,	bottom change change crystals homogenous	Color at No No Solid. No crystals.	change change change crystals	Color at No No No Solid, No crystals,	bottom   change   change   crystals   homogenous	Scixia refle
	%wt ai Surfactant Triclopyr (5%)		50 FS3		25 FS3		3 FS3		10 ES3			50 FS1		25 FS1		3 FS1		00 FS1		'6 FS4		
	%wt ai %wi Glyphosate Tricl		18 4.50		18 2.25		18 1.13		18 000	-		18 4.50		18 2.25		1.13		18 0.00		18 6.76	<del></del>	
	Formulation CODE G		F12X		F13X		F14X		EOX	<u></u>		F12M		F13M		F14M		FOM		F15C		

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	_		_			_					_
No crystals,	bottom  change  change  change  crystals homogenous	after mixing	Solid, No crystals,	change  change  crystals homogenous	after mixing	Solid, No crystals,	change  change  crystals homogenous	after mixing	Solid, No crystals,	change  change  change  crystals homogenous	after mixing
Solid,	crystals		Solid,	crystals		Solid,	crystals		Solid,	crystals	
ON	change		No	change		No	change		٥N	change	)
No	change		No	change		oN	change		oN	change	
ON	change		No	change		ON	change		No	change	)
Color at	bottom		Color at No	bottom		Color at No No	bottom		Color at No No No	bottom	
	change		No	change			change			change	•
FS4 No			FS4			FS4 No			FS3 No		
4.50			2.25			1.13			00.0		
18			18		8	18			18		
F12C			F13C			F14C		Į	FOM		,

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Table 2.1B. Stability Results.

CODE	% wt ai	Surfactant	-20/+20°C	,, , , , , , , , , , , , , , , , , , ,	60°C
	Triclopyr				
F6X	2.66	FS3	crystals	All formulations	No
				layered from freeze	layering
				thaw	
F3X	2	FS3	clear	All formulations	No
				layered from freeze	layering
				thaw	
F4X	3	FS3	crystals	All formulations	No
				layered from freeze	layering
				thaw	
F6M	2.66	FS1	crystals	All formulations	No
		]		layered from freeze	layering
				thaw	
F3M	2	FS1	clear	All formulations	No
				layered from freeze	layering
				thaw	
F4M	3	FS1	crystals	All formulations	No
				layered from freeze	layering
		-		thaw	
F6Y	2.66	FS5	clear	All formulations	No
				layered from freeze	layering
				thaw	
F3Y	2	FS5	clear	All formulations	No
				layered from freeze	layering
				thaw	
F4Y	3	FS5	clear	All formulations	No
				layered from freeze	layering
				thaw	
F7Z	4	FS5+NMP	crystals	All formulations	No
				layered from freeze	layering
				thaw .	

SECTION 3. GREENHOUSE TEST & RESULTS.

Objective: Greenhouse study of potential Roundup Brushkiller formulations on Red Maple and Red Oak.

Materials & Methods: Standard post emerge herbicide application procedures were used, such the procedure described below. The herbicide formulations tested are listed in Table 3.1 below. Additional information is available in Tables 1.1 and 1.2.

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Seeds of the plant species indicated were planted in 3.5 in square pots in a soil mix which was previously steam sterilized and prefertilized with a 14-14-14 NPK slow release fertilizer at a rate of 100 g/ft<sup>3</sup>. The pots were placed in a greenhouse with sub-irrigation. About one week after emergence, seedlings were thinned as needed, including removal of any unhealthy or abnormal plants, to create a uniform series of test pots.

The plants were maintained for the duration of the test in the greenhouse where they received a minimum of 14 hours of light per day. If natural light was insufficient to achieve the daily requirement, artificial light with an intensity of approximately 475 microeinsteins was used to make up the difference. Exposure temperatures were not precisely controlled but averaged about 27 °C during the day and about 21 °C during the night. Plants were sub-irrigated throughout the test to ensure adequate soil moisture levels.

Pots were assigned to different treatments in a randomized experimental design with 6 replications. A set of pots was left untreated as a reference against which effects of the treatments could later be evaluated.

Application of glyphosate compositions was made by spraying with a track sprayer fitted with a flateven 8008E nozzle calibrated to deliver a spray volume of 1348 liters per hectare (I/ha) at a pressure of 165 kilopascals (kPa). After treatment, pots were returned to the greenhouse until ready for evaluation. Treatments were made using dilute aqueous compositions.

For evaluation of herbicidal effectiveness, all plants in the test were examined by a single practiced technician, who recorded percent control, a visual measurement of the effectiveness of each treatment by comparison with untreated plants. Control of 0% indicates no effect, and control of 100% indicates that all of the plants are completely dead. Control of 85% or more is in most cases considered acceptable for normal herbicide use; however in greenhouse tests such as those for the examples it is normal to apply compositions at rates which give less than 85% control, as this makes it easier to discriminate among compositions having different levels of effectiveness. The reported % control values represent the average for all replicates of each treatment.

Table 3.1: Glyphosate Formulations for Greenhouse Testing:

Formulation	w/w %	w/w %	Amt., g	Salt	Surfact.	Amt	Other	Triclopyr
Code	Glyph.	Glyph.	ae/L	Form		surfact.	active;	amt %ai
	ae	ai				w/w %	Triclopyr	0.5
F3X	13.34	18.00	143.70	IPA	FS3	5.0%	Hammer	2.0%
F2X	13.34	18.00	143.27	IPA	FS3	5.0%	Hammer	1.0%
F1X	13.34	18.00	143.07	IPA	FS3	5.0%	Hammer	0.5%

F0X	13.34	18.00	142.78	IPA	FS3	5.0%		
F3M	13.34	18.00	143.60	1PA	FS1	5.0%	Hammer	2.0%
F2M	13.34	18.00	143.18	IPA	FS1	5.0%	Hammer	1.0%
F1M	13.34	18.00	142.96	IPA	FS1	5.0%	Hammer	0.5%
FOM	13.34	18.00	142.75	IPA	FS1	5.0%		
F4C	13.34	18.00	143.69	IPA	FS4	5.0%	Hammer	3.0%
F3C	13.34	18.00	143.26	IPA	FS4	5.0%	Hammer	2.0%
F2C	13.34	18.00	142.84	IPA	FS4	5.0%	Hammer	1.0%
F1C	13.34	18.00	142.63	IPA	FS4	5.0%	Hammer	0.5%
F0C	13.34	18.00	142.83	IPA	FS4	5.0%		-

COMME	RCIAL_	ACTIVE	<u>%Ai</u>
PRODUC	CTS		
RUP BSI	K CONC	GLYPH	27.0
BBG		TRICL	8.0
ENF BSI	CONC	TRICL	8.8

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Results: Table 3.2A

D OAK	OAK AVE.	15.0	20.0	57.5	5.0	27.5	10.0	17.5	12.5	45.0	12.5	
E AND RE	OAK REP 2	30.0	40.0	70.0	5.0	10.0	10.0	30.0	20.0	10.0	20.0	
RED MAPL	OAK REP 1	0.0	0.0	45.0	5.0	45.0	10.0	5.0	5.0	80.0	5.0	
TIONS ON	MAPLE AVE.	50.0	30.0	30.0	6.7	65.0	43.3	35.0	35.0	58.3	50.0	
FORMULA 5 DAT	MAPLE REP 3	65.0	40.0	20.0	10.0	70.0	70.0	25.0	30.0	65.0	40.0	
SHKILLER % CTRI	MAPLE REP 2	30.0	20.0	50.0	5.0	70.0	35.0	50.0	35.0	55.0	55.0	
JNDUP BRL	MAPLE REP 1	55.0	30.0	20.0	5.0	55.0	25.0	30.0	40.0	55.0	55.0	
TENTIAL ROI	MIX RATE 02/GAL	9	9	9	9	9	9	9	9	9	9	
rudy of PC	FORM	SL										
GREENHOUSE STUDY OF POTENTIAL ROUNDUP BRUSHKILLER FORMULATIONS ON RED MAPLE AND RED OAK	CHEMICAL FORMULN	F3X	F2X	F1X	F0X	F3M	F2M	F1M	FOM	F4C	F3C	
able 3.2A GREE	TRT	-	2	က	4	2	9	7	8	0	10	

75.0 5.0 <b>40.0</b>	5.0 10.0 7.5	0.0 5.0 2.5	0.0 70.0 <b>35.0</b>		45.0 50.0 <b>47.5</b>			10.0 5.0 7.5		<b>0.0</b> 0.0 <b>0.0</b>		
41.7	30.0	10.0	28.3		51.7			26.7		0.0		
50.0 35.0	35.0 20.0	5.0 10.0	25.0 30.0		 75.0 20.0			25.0 30.0		0.0 0.0		
40.0	35.0	15.0	30.0		0.09			25.0		0.0		
SL 6	SL 6	SL 6	9 TS		SL 4			SL 4				
F2C	F1C 8	FOC	RUP BSK 8	CONC	ORTHO	BBG		ENF BSK S	CONC	-\n	TREATED	IOGTINO
1	12	13	 14		15		_	16		17	н .	

Table 3.2B

RED OAK	21 DAT	OAK AVE.		97.5	100.0	100.0	0.06	0.06	95.0	0.66	81.5	94.0	
OLE AND F	% CTRL	OAK REP 2		100.0	100.0	100.0	100.0	100.0	95.0	0.66	88.0	100.0	
N RED MA		OAK REP 1		95.0	100.0	100.0	80.0	80.0.0	95.0	99.0	75.0	88.0	
ATIONS OF		MAPLE AVE.		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
FORMUL/	21 DAT	MAPLE REP 3		100.0	100.0	100.0	100.00	100.0	100.0	100.0	100.0	100.00	
SHKILLER	% CTRL	MAPLE REP 2		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
DUP BRU		MAPLE REP 1		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	,
ITIAL ROUN		MIX RATE 0Z/	GAL	9	9	9	9	9	9	9	9	9	
OF POTEN		FORM DESIG		SF	SL	SL	SL	SL	SL	SL	SL	SL	
GREENHOUSE STUDY OF POTENTIAL ROUNDUP BRUSHKILLER FORMULATIONS ON RED MAPLE AND RED OAK		CHEMICAL		F3X	F2X	F1X	K04	F3M	F2M	F1M	FOM	F4C	
GREEN		TRT		1	2	3	4	5	9	7	8	6	

3	S.	9	100.0	100.0 100.0 0	100.0.0	100.0	0.06	100.0	95.0
F2C	SF	9	100.0	100.0 0	100.0	100.0	100.0	98.0	0.66
F1C	SL	9	100.0	100.0	100.0	100.0	0.66	99.0	99.0
FOC	SF	9	100.0	92.0	88.0	94.3	45.0	100.0	72.5
RUP BSK	TS >	9	100.0	100.0	100.0	100.0	100.0	95.0	97.5
CONC									
		:							
ORTHO BBG	3G ST	4	100.0	100.0	100.0	100.0	100.0.0	100.0	100.0
ENF BSK	TS >	4	100.0	100.0	100.0	100.0	100.0	100.0	100.0
CONC									
UNTREATED	ED		0.0	0.0	0.0	0.0	0.0	0.0	0.0
CONTROL									

#### Discussion:

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5 DAT: The maples exhibited more injury as the triclopyr level went up. The oaks responded more inconsistently than the maples in this regard. Formulation F1X provided the best control of oak at this rating. Only formulations F3M and F4C provided more injury than Ortho Brush-B-Gone (BBG) on maple. The surfactant FS4 proved to be slightly better overall than did the tallowamine formulation FS1. The other tallowamine FS3 was consistently weaker than both other surfactants.

The current Roundup 27% brushkiller formulation failed to provide the same level of injury as that of the Brush-B-Gone product. It did, however, outperform Enforcer (ENF) on both species.

21 DAT: The maples proved to be much easier to control than the oaks at this evaluation time. Only F0C (no triclopyr) failed to provide 100% control. The oak control went up as the triclopyr level decreased. The lowest level of triclopyr was the best on oak and all triclopyr-containing formulations appeared to perform better than glyphosate alone. Tallowamine formulation FS3 seemed to be the best surfactant on oak.

SECTIONS 4/5. FIELD TEST & RESULTS.

### Example 4.1.

Objective: Demonstrate that F3M and F5M formulations provide commercially acceptable weed control.

Materials and Methods: A Ready-To-Use F5M and concentrate F3M brush killer formulations were evaluated. F5M RTU is constructed as 1% glyphosate, isopropylamine salt and 0.10% triclopyr, triethylamine salt, while F3M concentration formulation is constructed as 18% a.i. glyphosate and 2% a.i. triclopyr.

Nine field trials were conducted at various geographic regions in the U.S. to evaluate poison ivy, poison oak, kudzu, and multiflora rose control when treated with F5M and F3M.

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Table 4.1.1 Location and Number of Brush Tests by Species.

Geographic Region	State		Primary S	Species Teste	d
		Poison	Poison	Multiflora	Kudzu
•		lvy	Oak	Rose	
			Numb	per of tests	
Mid-West	Illinois	1		1	
	Ohio	1			
Central	Missouri	1			
South	Alabama			1	1
	Mississippi	1			1
West	California		1		

The brush tests were conducted on preexisting brush infestations typically located along and within fence and tree lines during June through August. All brush species were well-established and exhibiting complete foliation of leaf tissue at the time of treatment.

Each test was established using a randomized complete block design (RCBD) with each of the formulations being applied to 3, 15 ft² plots. Equal volumes of formulation were applied to each plot either with a RTU Pull n' Spray® sprayer used to apply, the RTU F5M formulation a Roundup® Herbicide Sprayer to apply the concentrate F3M formulation. F5M was applied based on 1 gal of solution treats 300 sq ft (equivalent to145 gallons per acre) and the standard application volume for a spray to wet treatment. F3M concentrate formulation was applied at a rate of 6 oz/gallon spray to wet.

Brush control ratings were evaluated at 1, 3, 21 and 90 days after treatment (DAT). Visual assessment of formulation efficacy was assessed on a 0 to 100% scale based on brush control (chorosis, necrosis and kill) compared to the untreated plots. Values close to 0% indicate no visual presence of brush damage by a formulation, while values approaching 100% indicate complete kill of a brush species compared to untreated plots. In addition, values greater than 80% control indicate that a product is supplying the industry standard commercially acceptable weed/brush control.

To quantify differences in percent brush control among formulations for each weed species by observation date, Duncan's multiple range test was applied and evaluated at P = 0.05.

### Results:

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Table 4.1.2 F3M and F5M gave commercial control up to 90 DAT on Poison Ivy and Poison Oak.

				Poiso	n Ivy			F	Poison	Oak	*
						D	AT				
Trt.	Formuln.	1	3	7	21	90	1	3	7	21	90
						% C	ontrol			,	
1	F3M	6a	36a	94b	100a	100a	0a	10b	85a	100a	100a
2	F5M	7a	36a	96a	100a	100a	0a	23a	80b	100a	100a
3	Untreated	0b	0b	0c	0b	0b	0a	0c	0с	0b	0b
	Check										

Means followed by same letter, for each weed species, do not significantly differ (P=0.05, Duncan's multiple range test)

Table 4.1.3. F3M and F5M gave commercial control up to 90 DAT on Multiflora Rose and Kudzu.

			Mι	ıltiflora	Rose				Kudz	u	
						D	AT				
Trt.	Formuln.	1	3	7	21	90	1	3	7	21	90
						% C	ontrol				
1	F3M	6a	34a	78a	93a	100a	11a	42b	70b	90a	88a
2	F5M	6a	46b	80a	94a	100a	10a	45a	85a	93a	90a
3	Untreated	0b	0c	0b	0b	0b	0b	0c	0с	0b	0b
	Check										

Means followed by same letter, for each weed species, do not significantly differ (P=0.05, Duncan's multiple range test)

Table 4.1.4. F3M and F5M gave commercial control up to 90 DAT on all brush tests combined.

			•		ll Brush <sup>1</sup>	
Trt.	Formuln.	1	3	7	21	90
				% C	Control	
1	F3M	6a	34b	86a	96a	98a
2	F5M	7a	39a	90a	97a	98a
3	Untreated	0b	0c	0b	0b	0b
	Chk					

<sup>1</sup>Four brush species were tested poison oak, poison ivy, multiflora rose, and kudzu across 9 brush tests

Means followed by same letter, for each weed species, do not significantly differ (P=0.05, Duncan's multiple range test)

#### 5 Discussion:

F5M and F3M provided commercial control of tough to control brush. At 90 DAT brush control for all species tested ranged between 90 and 100% control (Tables 4.2.1 through 4.3.4). F5M and F3M tested at various regions and brush species will deliver effective weed control of unwanted vegetation up to 90DAT.

# 10 Example 4.2. Evaluation on Poison Ivy.

Objectives: Evaluate various formulations on Poison Ivy.

Materials & Methods: Formulations tabulated below were field tested for 14 days in September to October at Clemson, South Carolina. See Tables 1.1 and 1.2 for description of product formulations.

## 15 Results: Table 4.2.1

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	1	
Product Form.	Rate in oz/1gallon	% injury 14 DAT Poison ivy
1. BSK	6oz	80
2. F1M	6 oz	80
3. F2M	6 oz	91.6
4. F4C	6 oz	100
5. F3M	6 oz	100
6. BBG	4 oz	70
7. BBG + FS1	4 oz + 3 oz	86.4
8. Untreated	0	10*
Check		

<sup>\*</sup> Untreated Check displayed some natural yellowing due to senescence, or aging.

Example 4.3. Evaluation on Kudzu.

Materials & Methods: Field evaluations of experimental formulations tabulated below were conducted on brush species (Kudzu Roadside) in Mississippi.

Table 4.3.1

1	-	•		
ı		٦	١	
		ı	,	
		1		

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Formulation	% ai Gly IPA	% ai Triclopyr	Surfactant	% Surfactant
Code		TEA		
F2M	18	1	FS1	5
F1M	18	0.5	FS1	5
F1C	18	0.5	FS4	5
F2C	18	1	FS4	5
F3M	18	2	FS1	5
F4C	18	3	FS4	5
BSK or RU1	27	0	FS1	?
BBG	0			0

### 15 Results: Table 4.3.2

Trt#	Form Code	Rate fl oz/gal	7DAT**	10DAT**	30DAT**
1	BSK	6	41.7	83.3	100
2	F1M	6	36.7	80	100
3	F2M	6	45	87	100
4	F4C	6	46.7	78.3	100
5	F3M	6	36.7	73.3	98.3
6	BBG	4	33.3	23.3	73.3
7	BBG + FS1	43	40	30	85
8	Untreated Check		0	0	0

\*\* Tabulated values are the mean of 3 tests.

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Example 4.4. Field Test at Mississippi #2.

Materials & Methods: Evaluations on experimental formulations were conducted on brush species at various locations and summarized below (*St Louis, Clemson SC, Mississippi*).

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Results: Table 4.4.1. Summary of Brush Tests

Location	Date	Formln	Formln				DAT				Weed
	First	Code		ď		10	17	16	30	42	
	Rated			כ	-	2	<u>†</u>	2	3	74	
St Louis	July	F3M	18+2	06				100		100	Poison Ivy
St Louis	July	F2M	18 + 1	80				100		100	Poison Ivy
St Louis	July	F1M	18 + 0.5	20				100		100	Poison Ivy
St Louis	July	F4C	18+3	92				100		100	Poison Ivy
St Louis	July	RU1	27% R'up	20				96		100	Poison Ivy
			Brush								
StLouis	July	BBG	Brush-B-Gone	85				100		100	Poison Ivy
St Louis	July	ENF	Enforcer	85				100		100	Poison Ivy
St Louis	July	F3M	18+2	85				100		100	Fesc/Blue
Louis	July	F2M	18+1	80		j		100		100	Fesc/Blue
St Louis	July	F1M	18 + 0.5	85				100		100	Fesc/Blue
St Louis	July	F4C	18+3	90				100		100	Fesc/Blue
St Louis	July	RU1	27% R'up	20				<u> </u>		100	Fesc/Blue
			Brush								
St Louis	July	BBG	Brush-B-Gon	20				99		20	Fesc/Blue
St Louis	July	ENF	Enforcer	20				15		0	Fesc/Blue
St Louis	July	F3M	18+2	80				86		100	Golden Rod
St Louis	July	F2M	18 + 1	65				88		86	Golden Rod

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Golden Rod	Golden Rod	Golden Rod		Golden Rod	Golden Rod	Fesc/Blue	Fesc/Blue	Fesc/Blue	Fesc/Blue	Fesc/Blue		Fesc/Blue	Fesc/Blue	Kudzu	Kudzu	Kudzu	Kudzu	Kudzu		Kudzu	Kudzu		
100	86	92		65	75	100	100	100	100	86		0	0										
												V		86	100	100	100	100		73	98		
85	86	92		99	75	100	100	100	100	98		0	0										
	ï																						
														73	87	80	82	83		23	30		
														37	45	37	47	42		33	40		
35	90	20		40	30	80	20	50	20	85		0	0										
18 + 0.5	18 + 3	27% R'up	Brush	Brush-B-Gon	Enforcer	18+2	18 + 1	18 + 0.5	18 + 3	27% R'up	Brush	Brush-B-Gon	Enforcer	18 + 2	18 + 1	18 + 0.5	18 + 3	27% R'up	Brush	Brush-B-Gon	Brush-B-Gon	+	
F1M	F4C	RU1		988	ENF	F3M	F2M	F1M	F4C	RU1		BG	ENF	F3M	F2M	F1M	F4C	RU1		988	J+988	S1	
July	July	July		July	July	July	July	July	July	July		July	July	October	October	October	October	October		October	October BBG+F		
St Louis	St Louis	St Louis		St Louis	St Louis	St Louis	St Louis	St Louis	St Louis	St Louis		St Louis	St Louis	Miss	Miss	Miss	Miss	Miss		Miss	Miss		

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Clem	October RU1	RG.	27% R'up	-	8 —		Poison Ivy
			Brush				
Clem	October	F1M	18 + 0.5		8		Poison lvy
Clem	October	F2M	18 + 1		91.6	9	Poison lvy
Clem	October	F4C	18 + 3		100	0	Poison lvy
Clem	October	BBG	Brush-B-Gon		02		Poison lvy
Clem	October BBG+F	BBG+F	Brush-B-Gon		86.4	4	Poison Ivy
		S1	+				
Clem	October	F3M	18 + 2		100	0	Poison lvy

Table 4.4.2: Grand Brush Test Summary

Location	Prod	Formuln	DAT						Weed		
	Code		5	7	70	14	16	30	42		
St Louis	F1M	18+0.5	70				100		100	Poison Ivy	
St Louis	F1M	18+0.5	85				100		100	Fesc/Blue	
St Louis	F1M	18+0.5	35			<u> </u>	85		100	Golden Rod	
St Louis	F1M	18+0.5	50				100		100	Fesc/Blue	
Miss	F1M	18+0.5		37	80			100		Kudzu	
Clem	F1M	18+0.5				80			_	Poison Ivy	
			60				96.3				
St Louis	F2M	18+1	80				100		100	Poison Ivy	
St Louis	F2M	18+1	80				100		100	Fesc/Blue	
St Louis	F2M	18+1	65				88		98	Golden Rod	
St Louis	F2M	18+1	70				100		100	Fesc/Blue	
Miss	F2M	18+1		45	87			100		Kudzu	
Clem	F2M	18+1				91.6				Poison Ivy	
•			74				97				
St Louis	F3M	18+2	90				100		100	Poison Ivy	
St Louis	F3M	18+2	85				100		100	Fesc/Blue	
St Louis	F3M	18+2	80				98		100	Golden Rod	
St Louis	F3M	18+2	80				100		100	Fesc/Blue	
Miss	F3M	18+2		37	73			98		Kudzu	
Clem	F3M	18+2				100				Poison Ivy	
			84				99.5				
St Louis	F4C	18+3	95				100		100	Poison Ivy	
St Louis	F4C	18+3	90				100		100	Fesc/Blue	
St Louis	F4C	18+3	90				98		98	Golden Rod	
St Louis	F4C	18+3	70				100		100	Fesc/Blue	
Miss	F4C	18+3		47	78			100		Kudzu	
Clem	F4C	18+3				100				Poison Ivy	
			86				99.5				
St Louis	RU1	27%	50				95		100	Poison Ivy	
		R'up									
		Brush									
St Louis	RU1	27%	50				95	<u> </u>	100	Fesc/Blue	
		R'up									
		Brush									
St Louis	RU1	27%	50				95		95	Golden Rod	
		R'up									
		Brush									

St Louis	RU1	27%	85		<u> </u>		98		98	Fesc/Blue
		R'up								
		Brush								
Miss	RU1	27%		42	83			100	,	Kudzu
		R'up								
		Brush								
Clem	RU1	27%				80				Poison Ivy
		R'up							1	
		Brush	:							
			59				95.8			
St Louis	BBG	Brush-	85				100		100	Poison Ivy
		B-Gon								
St Louis	BBG	Brush-	50				65		70	Fesc/Blue
		B-Gon								
St Louis	BBG	Brush-	40			-	65		65	Golden Rod
		B-Gon								
St Louis	BBG	Brush-	0				0		0	Fesc/Blue
		B-Gone								
Miss	BBG	Brush-		33	23			73		Kudzu
		B-Gone								
Clem	BG	Brush-				70				Poison Ivy
		B-Gone							:	
			44				57.5			
Miss	BBG+	Brush-		40	30			85		Kudzu
	FS1	B-Gone								
		+								
Clem	BBG+	Brush-				86.4				Poison Ivy
	FS1	B-Gone								
		+			:					
St Louis	ENF	Enforcer					100		100	Poison Ivy
St Louis	ENF	Enforcer					15		0	Fesc/Blue
St Louis	ENF	Enforcer					75		75	Golden Rod
St Louis	ENF	Enforcer	0				0		0	Fesc/Blue
	L		34	L	L		47.5		L	

10

15

20

25

Product	5	7	10	14	16	30	42	Weed
Code	DAT							
BBG	85				100		100	Poison Ivy
BBG	50				65		70	Fesc/Blue
BBG	40				65		65	Golden Rod
BBG	0				0		0	Fesc/Blue
BBG		33	23			73		Kudzu
BBG				70				Poison Ivy
RU1	50				95		100	Poison Ivy
RU1	50				95		100	Fesc/Blue
RU1	50				95		95	Golden Rod
RU1	85				98		98	Fesc/Blue
RU1		42	83			100		Kudzu
RU1				80				Poison Ivy
F3M	90				100		100	Poison Ivy
F3M	85				100		100	Fesc/Blue
F3M	80				98		100	Golden Rod
F3M	80				100		100	Fesc/Blue
F3M		37	73			98		Kudzu
F3M				100				Poison Ivy

Example 5. Additional Field Test in St. Louis

Following the procedures set forth in Example 4, additional fields tests were carried in the St. Louis area in July of 2003, in order to further evaluate the performance of various formulations on poison ivy, as well as all weeds present. (See Tables 1.1, 1.2 and 3 for additional details on product formulations.) The results of these tests are presented in Table 5, below.

Table 5: Summary of Test Results

Formuln	Formin	Rate in	Poiso	n Ivy	Total weed		
Code		oz/1gallon	% injury		% injury		
			6 DAT 12 DAT		6 DAT	12 DAT	
SBK	Super BK 32	3.2	60	90	50	65	
SPC	Spectra conc	5	70	94	70	80	
ENF	Enforcer	2.56	65	90	55	60	
BBG	Brush-B-Gon	4	60	85	55	60	
F3M	18 + 2	6	90	100	90	96	
F5M	1 + 0.1	RTU	85	100	85	96	
RUP	R'up RTU	RTU	80	99	80	94	
RU1	27% R'up Brush	6	90	90	80	85	